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A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, F.R.S., &c.

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THE CHEMICAL NEWS.

VOLUME LXXXIII.

EDITED BY SIR WILLIAM CROOKES, F.R.S., &c.

No. 2145.—JANUARY 4, 1901.

ON THE SPECTRUM OF THE MORE VOLATILE GASES OF ATMOSPHERIC AIR, WHICH ARE NOT CONDENSED AT THE TEMPERATURE OF LIQUID HYDROGEN.*

(PRELIMINARY NOTICE).

By Professor G. D. LIVEING, M.A., D.Sc.,
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and
Professor DEWAR, M.A., LL.D.,
Fullerian Professor of Chemistry, Royal Institution, London.

In August last some tubes were filled at low pressure by an improved process with the more volatile gases of the atmosphere.† The air was liquefied directly from that above the roof of the Royal Institution by contact at atmospheric pressure with the walls of a vessel cooled below -200° C. When about 200 c.c. of liquid had condensed, communication with the outer air was closed by a stop-cock. Subsequently, communication was opened, through another stop-cock, with a second vessel cooled by immersion in liquid hydrogen, and a part of the liquid from the first vessel, maintained at -210°, was allowed to distil into the second still colder vessel. When about 10 c.c. had condensed in the solid form in the second vessel, communication with the first vessel was cut off, and a manometer showed a pressure of gas of about 10 to 15 m.m. of mercury.

This mixture of gases was passed into tubes previously exhausted by a mercury pump, but before reaching the tubes it had to pass through a U-tube immersed in liquid hydrogen so as to condense less volatile gases, such as argon, nitrogen, oxygen, or carbonic oxide, which might be carried along by those more volatile. Previous trials with tubes filled in the same way, except that the U-tube in liquid hydrogen was omitted, showed that these tubes contained traces of nitrogen, argon, and compounds of carbon. The tubes filled with gas which had passed through the U-tube showed on sparking no spectrum of any of these last-mentioned gases, but showed the spectra of hydrogen, helium, and neon brilliantly, as well as a great many less brilliant rays of unknown origin. In addition, they showed at first the brightest rays of mercury, derived, no doubt, from the mercury pump by which they had been exhausted before the admission of the gases from the liquefied air. After some sparking the mercury rays disappeared, probably in consequence of absorption of the mercury by the electrodes, which were of aluminium.

In one experiment the mixture of gases in the second vessel, into which a fraction of the liquefied air was distilled as above described, was pumped out without being passed through the U-tube in liquid hydrogen and examined. This mixture was found to contain 43 per cent of hydrogen, 6 per cent of oxygen, and 51 per cent of other gases—nitrogen, argon, neon, helium, &c.—and it was explosive when mixed with more oxygen. This shows conclusively that hydrogen in sensible proportion exists in the earth's atmosphere, and if the earth cannot retain hydrogen or originate it, then there must be a continued accession of hydrogen to the atmosphere (from interplanetary space), and we can hardly resist the conclusion that a similar transfer of other gases also must take place. The tubes containing the residue of atmospheric gases uncondensed at the temperature of liquid hydrogen we have examined spectroscopically.

On passing electric discharges through them, without any condenser in the circuit, they glow with a bright orange light, not only in the capillary part, but also at the poles, and at the negative pole in particular. The spectroscope shows that this light consists in the visible part of the spectrum chiefly of a succession of strong rays in the red, orange, and yellow, attributed to hydrogen, helium, and neon. Besides these, a vast number of rays, generally less brilliant, are distributed through the whole length of the visible spectrum. They are obscured in the spectrum of the capillary part of the tube by the greater strength of the second spectrum of hydrogen, but are easily seen in the spectrum of the negative pole, which does not include the second spectrum of hydrogen, or only faint traces of it. Putting a Leyden jar in the circuit, while it more or less completely obliterates the second spectrum of hydrogen, also has a similar effect on the greater part of these other rays of, as yet, unknown origin. The violet and ultra-violet part of the spectrum seems to rival in strength that of the red and yellow rays, if we may judge of it by the intensity of its impressions on photographic plates. We were surprised to find how vivid these impressions are up to a wave-length 314, notwithstanding the opacity of glass for rays in that part of the spectrum. The photographs were taken with a quartz calcite train, but the rays had to pass through the glass of the tube containing the gases.

We have made approximate measurements of the wave-lengths of all the rays which are sufficiently strong to be seen easily or photographed with an exposure of thirty minutes, and give a list of them below. These wave-lengths are computed to Rowland's scale, and were deduced from the deviations produced by two prisms of white flint glass for the visible, and of calcite for the in-

* A Paper read before the Royal Society, December 13, 1900.

† In this paper we describe researches in continuation of those previously communicated to the Society by one of us, in a paper entitled "Application of Liquid Hydrogen to the Production of High Vacua, together with their Spectroscopic Examination," *Roy. Soc. Proc.*, vol. lxiv., p. 231.

visible, rays. The wave-lengths assigned to the helium lines are those given by Runge and Paschen, and some of these lines were used as lines of reference. In general, the iron spark spectrum was the standard of reference.

The tubes when first examined showed the lines of the first spectrum of hydrogen vividly, and the earlier photographs of the spectrum of the negative pole contained not only the violet lines of hydrogen, but also the ultra-violet series as far up as λ 337. In order to get impressions of the fainter rays, exposures of half-an-hour or more were required, and a succession of photographs had to be taken so as to get different sections of the spectrum into the middle of the field, where measurement of the deviations would not be impeded by the double refraction of the calc spar. As the light of the negative pole only was required, the electric discharge was made continuously in one direction only, with the result that the hydrogen lines grew fainter in each successive photograph, and soon disappeared altogether. Along with the ultra-violet rays the less refrangible rays of hydrogen also disappeared, so that no trace of the C or F line could be seen, nor yet of the second spectrum, so long as the current passed in the same direction as before. Reversal of the current soon made the F line show again, so that it seems that the whole of the hydrogen was driven by the current to the positive pole. The conditions under which this ultra-violet series shows itself are a matter of interest. It appears here in the midst of a brilliant spectrum due to gases other than hydrogen, and yet it is very difficult to obtain a photograph of it when no gas but hydrogen is known to be present, or, at least, to become luminous in the electric discharge.

We have had an opportunity of comparing the spectrum of the volatile residue of air with that of the more volatile part of gas from the Bath spring. The tube did not admit of the separate examination of the light from the negative pole, but was examined end on, so that the radiation probably included rays emitted from the neighbourhood of the negative pole. The whole of the hydrogen had been removed from the Bath gas, but not all the argon. In the spectrum of this gas the rays of helium are dominant, decidedly stronger than those of neon, although the latter are very bright. In the spectrum of the residue of atmospheric air, the proportion of helium to neon seems reversed, for in this the yellow neon line is as much more brilliant than the yellow helium line as the latter is more brilliant in the spectrum of Bath gas. All the prominent lines in the spectrum of the volatile residue of Bath gas were also in that of the residue of atmospheric air except the argon lines. There were, on the other hand, many lines in the latter not traceable in the former, some of them rather conspicuous, such as the ray at about λ 4664. It is, of course, probable that such rays are the outcome of some material not contained in the Bath gas. A very conspicuous pair of lines appears in photographs of the spectrum of the air residue, at about λ 3587, which is not traceable in the spectrum of Bath gas. The helium line, λ 3587·4, is seen in the latter spectrum, but is quite obscured in the former spectrum by the great intensity of the new pair. This helium ray is really a close double, with the less refrangible component much the weaker of the two, but the new pair are wider apart, and of nearly equal intensities; this character also distinguishes them from the strong argon line at λ 3588·6. They are, however, very much more intense at the negative pole than in the capillary, and it will require a good deal more study to determine whether these rays, and many others which we have not tabulated, are due to the peculiarity of the stimulus at the negative pole, or to the presence of a previously unrecognised material.

As our mixture of gases probably includes some of all such gases as pervade interplanetary and interstellar space, we early looked in their spectra for the prominent nebular, coronal, and auroral rays. Searching the spectrum about λ 5007 no indication of any ray of about that wave-length was visible in the spectrum of any one of the three tubes which had been filled as above described. Turning to the other green nebular line at about λ 4959 we found a weak rather diffuse line to which our first measure assigned a wave-length 4958. The correctness of this wave-length was subsequently verified by measuring with a micrometer eye-piece the distances of the line from the helium lines λ 4922·1 and λ 5015·7 which were in the field of view at the same time. The position of the line was almost identical with that of the iron spark line λ 4957·8, and the conclusion arrived at was that the wave-length was a little less than 4958, and that it could not be the nebular line. There remained the ultra-violet line λ 3727. Our photographs showed a rather strong line very close to the iron spark line λ 3727·8, but slightly more refrangible. As the line is a tolerably strong one it could be photographed with a grating spectrograph along with the iron lines. This was done, and the wave-length deduced from measuring the photograph was 3727·4. This is too large by an amount which considerably exceeds the probable errors of observation, and we are forced to conclude that the nebular material is either absent from our tubes, or does not show itself under the treatment to which it has been subjected.

Although the residual gases of the atmosphere uncondensed at the temperature of liquid hydrogen do not show the nebular lines, we found that another tube gave a ray very close indeed to the principal green nebular ray. This tube had been filled with gas prepared in the same way as the others, with the exception that, in passing from the vessel into which the first fraction of liquid air was distilled, it was not passed through a U-tube immersed in liquid hydrogen on its way to the exhausted tube. In consequence it contained traces of nitrogen and argon, and when sparked showed the spectra of these elements as well as those of hydrogen, helium, &c. The nitrogen spectrum disappeared after some sparking, but the tube still shows rays of argon as well as those of the gases in the other tubes. On examining the spectrum of the negative pole in the neighbourhood of the principal nebular green ray, a weak ray was seen in addition to those given by the other tubes. It was found by comparison with the nitrogen rays λ 5002·7 and λ 5005·7 to be a little less refrangible than the latter of these rays, and by measuring its distance from the nitrogen rays and from the two helium rays λ 4922·1 and λ 5015·7 with a micrometer eye-piece, the wave-length λ 5007·7 for the new ray was deduced. This looks as if we might find the substance which is luminous in nebulæ to be really present in the earth's atmosphere, and we hope shortly to be able to verify the observation of it.

(To be continued).

DETECTION OF ARSENIC IN THE PRESENCE OF SULPHITES, &c.

By JAS. F. SMITH.

WHEN sulphuretted hydrogen and arseniuretted hydrogen are heated together a mutual reaction occurs; the products so obtained are sulphide of arsenic, sulphur, and free hydrogen.

This takes place when the gases are passed slowly through a tube heated to redness, as in Marsh's test for arsenic; it is also deposited from the flame when the mixed gases are burnt, and a piece of cold porcelain is brought into it.

The above reaction therefore forms a convenient method for the detection of arsenic in the presence of compounds of sulphur that give off sulphuretted hydrogen when treated with zinc and acid, not only in inorganic solutions, but extracts similar to beer, without previous treatment. The experiment is conducted in Marsh's apparatus, and in the same way, the only difference being in the results

obtained in the heated tube, or on cold porcelain, as above stated.

The following precautions, however, are necessary to obtain all the arsenic as sulphide in the heated tube. To add the solution under examination slowly and in small quantities of about 1 to 2 c.c. at a time to the acid and zinc, in the generating flask, and to keep the heated tube at red heat for about 1 inch in the centre, otherwise some loss may take place.

When cold the deposit is washed with a little carbon bisulphide to remove the free sulphur, and afterwards with a little sodium, potassium, or ammonium hydrate to dissolve out the sulphide of arsenic, and the tube washed with a few drops of water, two or three times, adding the washings to the solution containing the sulphide of arsenic; neutralise with hydrochloric acid, and if the quantity of precipitate is large it can be filtered off and tested by the usual methods, but if the solution is only slightly coloured yellow it must be evaporated and a few drops of strong nitric acid added and again evaporated to dryness on a water-bath, the residue taken up with a few drops of hot water, and tested by Marsh's method in the usual way.

By this, 15 parts of arsenic in 1,000,000 were detected in the presence of a large quantity of bisulphite in 5 c.c. of beer without previous treatment.

When the amount of sulphuretted hydrogen evolved is too small to effect the precipitation of all the arsenic, the sulphide is first precipitated nearest the heated part, and after the yellow sulphide a metallic deposit of arsenic, or if the gas is burnt at the end of the tube—which, of course, must not be heated—and a piece of cold porcelain is brought into the flame, there will be a yellow deposit of sulphur and sulphide of arsenic with a metallic ring round the edge of it; this can easily be tested after the removal of the sulphur and sulphide of arsenic.

The above has also been applied to antimony, which undergoes the same mutual decomposition under the same conditions; its detection and separation from arsenic can easily be carried out, as the antimony sulphide is deposited nearer the flame than that of arsenic, and sometimes a distinct line separates the two sulphides.

The antimony sulphide can easily be removed by means of dry hydrochloric acid gas after the removal of the free sulphur, and the remaining sulphide of arsenic treated as above, or the separation can be effected by any of the well known methods.

30, Chester Road, Akroydon,
Halifax.

ON THE DIVISION OF NITROGEN IN CHEMICAL MANURE COMPOUNDS.

By J. OSTERSETZER, F.I.C., F.C.S.

In an article on "Nitrogen in Artificial Manures" published in 1884 (CHEMICAL NEWS, vol. l., p. 291), I have shown, by a series of laboratory experiments, how far organic nitrogen can be made soluble by the action of sulphuric acid. In the manufacture of chemical manure compounds, it is neither possible nor would it appear desirable to carry the point for dissociating nitrogenous matter to its theoretical limit. There is, however, no doubt that more or less considerable quantities of ammonium sulphate can be detected in dissolved manure compounds which derive their nitrogen from organic sources only. I have recently examined several samples of such manures and obtained the following results, viz.:—

No.	Percentage of the N made soluble.	Percentage of the N left insoluble.
I.	23·16	76·84
II.	38·30	61·70
III.	25·15	74·85
IV.	36·91	63·09
V.	28·80	71·20
VI.	29·89	70·11

It will be seen from the foregoing that, in addition to organic nitrogen homogeneously divided, a certain percentage of ammonium sulphate is thus introduced, but in a state of molecular division; that is to say, more minute than can be obtained by mechanical means, and certainly more intimate than by the rough and ready addition of commercial ammoniacal salts to superphosphate, as is frequently practised by agriculturalists when compounding their own formulæ.

This question of division has of late attracted an increased amount of attention from a theoretical as well as a practical point of view. It has frequently been found that some of the misleading—if not negative—results obtained on experimental plots could be traced to the want of homogeneous division of fertilisers; when, for instance, a thin layer of superphosphate or that of other ingredients was proved to retard the action of ammonium sulphate (J. M. Pomorski, *Zeit. Landw. Versuchs. w. Oesterr.*, 1900, iii., 649).

The chemical composition will, of course, remain the most important factor in estimating the relative value of manures, but, judging from the present current of opinion, such valuations on the one hand, and the actual methods for practical experiments on the other, will have to be supplemented by the careful investigation of the *state of division* in all its aspects.

Goulding's Manure Works, North Wall, Dublin,
December 21, 1900.

THE EFFECT OF SMALL AMOUNTS OF ARSENIC ON COPPER.

By ERNEST A. LEWIS.

The following experiments on the influence of small amounts of arsenic on the strength of copper were made by the writer, as the metallurgical and chemical text-books and journals do not appear to give any information on this subject. In Hiorn's "Metallic Alloys" it is stated that "Copper and arsenic readily combine when metallic arsenic is dropped into molten copper. When a very small quantity is thus added, the metal may be cast into a sound ingot, which contracts during solidification like phosphorised copper, and may be rolled cold and afterwards drawn into fine wire. Much arsenic is highly injurious, making the metal hard and brittle." The copper used contained—

Copper	99·843	per cent.
Oxygen	0·05	,,
Arsenic	0·007	,,

The arsenic used was commercial arsenic, containing 99½ per cent arsenic.

Six experiments were made as follows:—

Eight lbs. of copper were melted in a crucible, and to it was added enough arsenic to give the following percentages of arsenic. The copper was then cast into a test-piece, and rolled down to ¼th inch thick.

The sheets were put in cold water whilst still red-hot to scale them.

Photomicrographs were made of each of the samples of cast-metal before rolling.

	Arsenic added. Per cent.	Arsenic found in copper. Per cent.
1.	2	1·80
2.	1½	1·37
3.	1	0·94
4.	¾	0·75
5.	½	0·53
6	¼	0·24

No 1 was found to contain 1·75 per cent arsenic after rolling; this shows that the re-heating of the metal before

rolling does not affect the amount of arsenic present to any extent.

1. Rolled well.
2. Rolled very well.
3. " "
4. Rolled well.
5. " "
6. " "

Pieces of the six rolled samples were bent over and hammered up closely, both hot and cold; there was not the sign of a crack in either of them.

Tensile Tests.

	Arsenic. Per cent.	Break, in tons per square inch.	Limit of elasticity. Tons per square inch.	Elongation. Per cent.
1.	2	17·83	11·52	20
2.	1½	18·83	10·09	28
3.	1	18·02	9·01	25
4.	¾	18·31	8·91	21
5.	½	18·38	9·52	29·5
6.	¼	16·92	10·25	27·5
Ordinary sheet copper .		13·4	7	25

From the above experiments, it appears that the presence of a small amount of arsenic in copper intended for rolling is an advantage, except the copper is intended for electrical purposes. The tensile strength is from 3 to 5 tons higher than ordinary sheet copper treated in the same way, and the limit of elasticity is about 3 tons per square inch higher, and the elongation is not reduced.

From the micrographical examination of arsenical copper, it appears to consist of crystals of copper surrounded by an eutectic, which is probably arsenide of copper or a solution of arsenide of copper in copper.

There is no advantage in having more than 0·5 per cent arsenic present.

310, Dudley Road, Birmingham,
December 17, 1900.

ON THE CAUSE OF ERROR IN THE SEARCH FOR SALICYLIC ACID IN WINES.

By A. Y. FERREIRA DA SILVA.

Several Portuguese wines recently, in Brazil, have been declared to be salicylised from the fact that analysis showed traces of salicylic acid.

In this connection the author has made some experiments on wines from this and other localities (de Bastao, de Monsao, &c.), with regard to which no suspicion could be entertained as to their genuineness.

They were treated by the German method (*Zeits. für Analytische Chemie de Fresenius*, xxxv., 1896), by operating on 50 c.c. (not more), of acidulated wine, which was shaken up with a mixture of equal volumes of ether and petroleum ether, or on 200 c.c. of wine which was shaken up with ether, adopting the method of Pellet, Grobert, and Baudrimont, which has been used in the laboratories of Brazil since 1888.

The German method has in no case given a violet colouration with perchloride of iron; that is to say, the results were always negative; at the same time the method is exact and delicate.

By the Pellet-Grobert method a pale rose, or a violet-red colour was obtained from several samples, which an unsuspecting analyst would certainly take as an indication of traces of salicylic acid.

This latter method is therefore one which may cause perfectly natural wines to be returned as salicylised, and is thus erroneous.

It is thus undeniable that in certain Portuguese wines a small quantity of a substance may be met with closely resembling salicylic acid, which can be extracted by means of ether in sufficient quantity to give a colouration with perchloride of iron, resembling that of salicylic acid, when a considerable volume of wine is used for the operation. This fact, which is new as regards Portuguese wines, will account for the results obtained in Brazil, and is in fact the true explanation.

They are not salicylised wines, but they naturally contain a small proportion of a substance resembling salicylic acid in its reactions.

At the meeting of German chemists at Erlangen, in 1890, Professor L. Medicus mentioned an exactly similar occurrence in the case of some Austrian and German wines. He was of the opinion, from experiments made, that the principle analogous to salicylic acid came from the grape stalks.

Whatever it may be, the fact is of great analytical importance.

If in the search for salicylic acid, in cases of supposed falsification, we make use of the Pellet, Grobert, Baudrimont, or other method, in which we have to use a considerable volume of wine, we run the risk of obtaining a coloured reaction, falsely resembling that of salicylic acid, and therefore of declaring as salicylised wines which do not merit that description.

We are thus in accord with Professor Medicus in recommending that in the search for salicylic acid, no more than 50 c.c. of wine should be taken, which is the volume indicated when using the official Austrian and German methods.

The sensitiveness of this process being greater than 1 per 200,000, we are perfectly able to detect 5 m.grms. of salicylic acid per litre, or 0·5 grm. per hectolitre, a quantity which is much less than that required for the conservation of wine (3 to 8 grms. per hectolitre). We may therefore rest assured that fraud will be detected by this process, and at the same time no errors will be committed.—*Bull. Soc. Chim.*, Series 3, xxiii., 795.

THE ESTIMATION OF MANGANIC ACID IN THE PRESENCE OF MANGANOUS SALTS BY MEANS OF ARSENIOUS ACID IN ALKALINE SOLUTION.

By T. REICHARD.

It often happens in making an analysis, that we have to estimate the manganous salts as well as those of manganic acid. In such a case as this, very good results can be obtained by making use of the arsenious acid process, previously described but slightly modified. If the solution contains manganates or permanganates, we add a certain quantity of soda-lye, so that the manganous salt will be completely precipitated in the form of manganous hydrate or manganoso-manganic hydrate. It is then only that we add the titrated solution of arsenious acid in excess. The residue, collected on a filter, is weighed. The difference between the total amount of manganese found by the gravimetric method, and that given by the volumetric method, represents the quantity of the metal which exists in the state of manganous salt, in the substance under examination.

We may also proceed in another different manner, subject, however, to starting with solutions as neutral as possible, and working in the absence of iron and chromium. This second method depends on the fact that the manganous salts are completely precipitated at about 80°, by permanganate of potash. Finally, a third method is founded on the precipitation of the manganous salts, in the form of arsenites, by alkaline solutions of arsenious acid, at the same time that the permanganate is decomposed. The products of decomposition, manganous hydrate and arsenite of manganese, are thrown on a filter,

and, in the filtered solution, the quantity of arsenious acid which has not taken part in the solution is estimated by means of a solution of iodine.

The contents of the filter are dissolved in sulphuric acid, and the amount of arsenious acid, existing in the form of arsenite of manganese, is estimated by means of a titrated solution of permanganate of potassium. The different figures thus obtained enable the proportion between the two compounds of manganese to be established.—*Chemiker Zeitung*, xxiii., p. 867.

ON AN EUCALYPTUS OIL CONTAINING SIXTY PER CENT OF GERANYL ACETATE.*

By HENRY G. SMITH, F.C.S.,
Assistant Curator, Technological Museum, Sydney.

IN this paper the author shows that the oil of *Eucalyptus macarthuri*, known locally as Paddy's River Box, is very rich in geraniol, it containing 60 per cent of geranyl acetate, and 10·64 per cent of free alcohol, calculated as geraniol. The oil is somewhat analogous with that obtained from *Darwinia fascicularis*, brought under the notice of this Society by Mr. R. T. Baker and the author in December, 1899. Both *Darwinia* and *Eucalyptus* belong to the natural order Myrtaceæ. The oil of *E. macarthuri* contains eudesmol (the stearoptene of Eucalyptus oil), the fraction distilling between 266—282° C., crystallising quite solid in the bottle. This substance is absent in the oil of *Darwinia*. The yield of oil from this Eucalypt, collected in October from near Wingello, in this colony, and obtained by steam distillation from fresh leaves and branchlets, was 0·112 per cent. The whole of the ester was saponified in the cold by alcoholic potash in one and a half hours. As no heat was applied, the separated oil was excellent, the geraniol not being interfered with. This fact of cold saponification of geranyl acetate might be used for quantitative determination of this ester, when it and other esters are present in essential oils. Citral was obtained by oxidation, and the pure geraniol prepared from the calcium chloride compound; this was a colourless oil boiling at 224—225° C. (uncor.), and had a specific gravity of 0·885 at 20° C. The acid of the ester was shown to be acetic acid. The crude oil contained neither eucalyptol nor phellandrene, it was entirely different in appearance and constituents from ordinary Eucalyptus oil. It formed a clear solution with two volumes of 70 per cent alcohol, it had an optical rotation of +3·6° in a 100 m.m. tube, and specific gravity at 15° C. of 0·9245, the comparatively high specific gravity being due to the presence of the stearoptene.

The Separation of Dithionic Acid from the other Acids of Sulphur.—A. Lingi and L. Bonavia.—The method proposed is based on the fact that all the lower acids, with the exception of dithionic acid, are oxidised in alkaline solution by permanganate or hypobromite of potassium. After oxidation the solution is acidulated with acetic acid, and the sulphuric acid precipitated by a very slight excess of acetate of baryta; let stand for some hours at 40° and filter. The filtrate is treated with aqua regia, or hydrochloric acid and potassic chlorate, and chloride of barium. After prolonged heating on the water-bath this fresh precipitate of sulphate of barium, formed from the dithionic sulphur, is collected.—*Gazz. Chim. Ital.*, p. 341.

* A Paper read before the Royal Society of New South Wales, November 7, 1900.

THE SEPARATION OF TUNGSTEN TRIOXIDE FROM MOLYBDENUM TRIOXIDE.*

By MAX J. RUEGENBERG and EDGAR F. SMITH.

THE separation of tungsten from molybdenum is always of interest to those who are brought in contact with analytical methods. It has been the subject of numerous investigations and much discussion, and while comparatively good methods exist for this purpose, the analyst continues to seek for others, hoping that eventually he shall find a procedure which will be satisfactory in all respects and under nearly all conditions.

The writers have not discovered the method *par excellence*, but desire to offer briefly, in the following lines, their experience in pursuing a suggestion made in an article emanating from this laboratory; viz., "tungstic acid is . . . . insoluble in concentrated or dilute sulphuric acid, hot or cold, whereas molybdenum trioxide is very easily and rapidly dissolved, so that we have in this deportment a very simple and exact method for the separation of the two metals" (En. D. Desi, *Journ. Amer. Chem. Soc.*, xix., 242).

No analytical data accompanied this declaration; therefore it seemed not improper to attempt to learn the conditions most favourable for the separation. Upon trial it was found that sulphuric acid of specific gravity 1·378, dissolved molybdenum trioxide very readily and apparently did not affect the tungsten trioxide. Acid of this concentration was therefore used with the following mixture of the two oxides:—

1. 0·7355 grm. of tungsten trioxide and 0·0185 grm. of molybdenum trioxide were digested for a few minutes with 25 c.c. of warm sulphuric acid. The insoluble portion was filtered out, and washed with water containing sulphuric acid. After drying, it was ignited and weighed. It equalled 0·7350 grm.

The other trials, conducted in precisely the same manner, were as follows:—

	II. Grms.	III. Grms.	IV. Grms.	V. Grms.	VI. Grms.
Tungsten trioxide taken	1·0638	0·0871	0·3588	0·8868	0·5996
Molybdenum trioxide taken	2·2712	0·6871	1·1836	1 1986	1·0770
Tungsten trioxide found	1·0630	0·0870	0·3587	0·8866	0·5996

The filtrate containing the dissolved molybdic acid showed no tungstic acid upon examination.

These results indicate that where the two oxides are present together this mode of separation is apparently of value and merits consideration.

A weighed quantity of a ferric salt equivalent to 5 grms. of ferric hydroxide was precipitated with ammonia water, and the resulting precipitate, after being washed, was mixed in a beaker with different amounts of tungsten trioxide, and the resulting mixture was then digested with sulphuric acid of the strength of that used in the preceding experiments. The residual oxide was treated as before:—

	I. Grms.	II. Grms.	III. Grms.	IV. Grms.	V. Grms.	VI. Grms.
Tungsten trioxide taken	0·5282	0·2087	1·3270	0·2004	0·9091	0·2263
Ferric hydroxide taken	5·0000	5·0000	5·0000	5·0000	5·0000	5·0000
Tungsten trioxide found	0·5278	0·2086	1·3265	0·2003	0·0988	0·2262

We may conclude from these trials that the solubility of the trioxide in the sulphuric acid is in no wise affected by the presence of the iron.

* Contribution from the John Harrison Laboratory of Chemistry. From the *Journal of the American Chemical Society*, vol. xxii., No. 11.

THE ALLOTROPIC FORMS OF SELENIUM.*

By A. P. SAUNDERS.

(Continued from vol. lxxxii., p. 310).

5. *Metallic Selenium.*

SOME of the methods by which this modification can be obtained from the other have been already indicated. It is in the mass a steel-grey metallic substance; when powdered, it gives a black powder, but if the grinding be made finer still, the substance is seen to be red. Thus, if a little of the powder be rubbed upon a soft porcelain plate, it becomes so red that it cannot be distinguished from the other forms in the same state of division. There are in the literature many conflicting statements regarding the powder and streak of this modification. Thus, Rathke (1869), states that it is black, even in the finest powder; and the streak is almost always given as black. Mitscherlich, on the other hand, observed that the streak was red. In my experiments on the changes of the amorphous form in liquids, I observed that the powder which results in quinoline and some of the other compounds used, while it appears black to the eye, always shows a purplish colour under the microscope; and it is easy to rub this into a red powder in the way indicated.

In view of the possibility of a reverse transformation from the metallic form back to the vitreous at lower temperatures, I made some experiments upon the red powder obtained from metallic selenium in order to show that it really retained the properties of that form. The first of such experiments was made with some of the powder out of quinoline, and was far from reassuring. I found that when this is rubbed up very fine, so that it is quite red, and then treated with carbon disulphide, it gives a coloured solution, indicating the presence of one of the soluble forms of selenium. The powder obtained from some grey metallic selenium, which had been prepared by heating the vitreous form for some time to 150°, gave the same result, although in this case the resulting colour was less intense. When selenium is dissolved in hot sulphuric acid to purify it, there is often a separation of crystals about the upper surface of the liquid. They are in the form of grey metallic scales, and as they separate at a high temperature, it was to be assumed that they would be quite free from the amorphous modification. When finely powdered, they also give a red powder, and this when brought into contact with carbon disulphide colours it, though only very slightly. Plainly, then, the purer the metallic modification is, the less soluble is its powder, in carbon disulphide; and I presume therefore, that if one could prepare the metallic modification in quite pure condition, it would no longer show this property at all. With regard to the presence of soluble selenium in the metallic form which was prepared from the vitreous substance, Petersen (1891), has observed the same thing. He found that the purest metallic selenium he could prepare always contained about 1 per cent of a form soluble in carbon disulphide.

The quantity of material used in the above tests was small, but it has been mentioned in speaking of soluble selenium that one part of that material in 10,000 parts of water imparted a distinct colour to the solution; hence the quantity of the soluble form which would be required to colour 1 or 2 c.c. of carbon disulphide would, without doubt, be extremely small.

In making some experiments upon the effect of heat on these red powders, I found it impossible to prepare one which did not turn grey on heating to about 200° in an air-bath; but on rubbing up again, even at that temperature, the red colour always reappears. This observation I am somewhat at a loss to explain. It is due, perhaps, to an alteration in the state of aggregation, but how this is brought about with a substance which melts sharply at 217° without previous softening, and in a powder which is a mixture of selenium and foreign matter, it would be difficult to say.

In addition to the method of preparation by direct transformation of the other forms, metallic selenium may be obtained by the spontaneous decomposition of solutions of the alkali selenides in contact with the air; it then forms a crust consisting of very small crystals, which were considered by Berzelius to be tetragonal.

Fabre (1887), mentions that selenium separates in the metallic form when hydrogen selenide is decomposed by moist oxygen. It is soluble in many organic liquids at high temperatures; in the dilatometer experiments recorded above, beautiful, leaf-like crystals were obtained on heating to 230° with quinoline, and cooling down. Ethyl benzoate, aniline, naphthalene, and other organic substances also dissolve it at high temperatures.

Fröbel (1840), made a microscopic study of the crystals which separate from a solution of ammonium selenide, and pronounced them to be orthorhombic.

The crystal form of metallic selenium has been studied by Muthmann (1890), who prepared the crystals by sublimation. Earlier observers had in most cases studied those crystals which separate from solutions of selenides of the alkalis, and in this way none were obtained of sufficient size to make measurements possible. Muthmann finds them hexagonal, rhombohedral, and fully isomorphous with tellurium. The observed faces were ∞R and R.

6. *Heat Conductivity.*

Bellati and Lussana (1887), observed that the heat conductivity of selenium was increased by illumination. They covered a circular plate of crystalline selenium with a double salt HgI_2CuI_2, and heated it at a point by means of a hot platinum wire. The double iodide is red at ordinary temperatures, brown above 70°, and hence the area of change of colour is a measure of the heat conductivity. They guarded against heating effects from the source of light, and found that direct sunlight increased the heat conductivity 8—25 per cent. Even the light of a gas flame had a perceptible effect.

7. *Heat of Transformation of Liquid Selenium into the Metallic Modification.*

The first determination of this heat value was made by Regnault (1856). The figures obtained by him have scarcely more than a qualitative value, but are quoted here for the sake of comparison with the later results of Petersen (1891).

Regnault's method was to place a mass of about 200 grms. of vitreous selenium in an oven at 100°. A thermometer standing in the selenium was then read every minute. When the temperature reached about 98° the substance began to go over to the metallic form, and the temperature rose to about 214°, subsequently dropping to 100°. The main corrections are (1) for the heat absorbed in the containing vessel, and (2) for the loss by radiation; the first of these is made on the basis of a previous determination of the water-equivalent of the vessel, the second by noting the normal rate of change per minute in the temperature of the selenium when no transformation was going on in the mass. Regnault reached the conclusion that the reaction set free enough heat to raise the temperature of the selenium from 98° to about 329°, *i.e.*, through 231°. A second determination was made by another method, which is even less exact, and the results so obtained indicated that the heat of reaction would raise the mass of selenium from 0° to 180°.

Regnault concludes that vitreous selenium in passing over to the metallic form sets free enough heat to raise its own temperature about 200°. In other words, taking the specific heat of vitreous selenium as 0·1, we have the value about 15 K for 1 grm.-equivalent of selenium.

Before passing on to consider the determination of Petersen we must mention the researches of J. Thomsen (*Thermochem. Unters.*, ii., 269, 313), which bear indirectly

* From the *Journal of Physical Chemistry*, vol. iv., No. 6.

upon this point, and are of especial interest in connection with a possible difference between the vitreous and amorphous forms of selenium. Thomsen determined firstly the heat involved in the reaction :—

$$SeO_2Aq + 2HClAq + 2NaSHAq = = 2NaClAq + 2H_2O + Se + S_2.$$

The solutions used had the molecular composition :—

A.. .. .. $NaSH + 616{\cdot}7\ H_2O$.
B.. .. .. $SeO_2 + 2HCl + 1500\ H_2O$.

In each experiment 1/30 of the corresponding weight of A and 1/60 of that of B was used.

The total heat value is made up as follows :—

$$R = \begin{cases} 2(NaOHAq, HClAq) - 2(NaOHAq, SH_2) \\ + 2(H_2,O) - 2(H_2,S) - (Se,O_2,Aq). \end{cases}$$

R is found experimentally to be 733·98 K; introducing this along with previously known values, we get—

$$733{\cdot}98 = 274{\cdot}80 - 249{\cdot}80 + 1367{\cdot}14 - 94{\cdot}80 - (Se,O_2,Aq).$$

whence $(Se,O_2,Aq) = 563{\cdot}36$. It will be seen from the nature of this reaction that the heat value here found refers to amorphous selenium.

Thomsen determined, secondly, the heat of formation of the chloride Se_2Cl_2 from "ordinary amorphous selenium, prepared by cooling the melted substance," *i.e.*, from the vitreous form.

Three separate determinations gave 221·29—219·85—223·35, the mean being 221·5. From the chloride Se_2Cl_2 he determined the heat of formation of the chloride $SeCl_4$, and finally, by finding the heat of reaction of this substance with water, obtained as an independent result for the reaction (Se,O_2,Aq), 559·86. Thomsen considers these two results in satisfactory agreement, although he suggests that a slight difference in the physical state of the selenium in the two cases may explain the variation. It is of interest to note that the difference is in the direction of greater heat of reaction for selenium in the amorphous state. This falls into line with what is said below in the chapter on specific gravities, regarding a possible difference between the two forms.

Fabre (1887), measured the heat of transformation of liquid selenium into crystalline, by placing the material in the calorimeter, and warming it by adding sulphuric acid to water in a larger tube, which surrounded the one containing the selenium; after the reaction was over, these tubes were broken, and a correction then introduced for the heat of dilution of the sulphuric acid in the total water-content of the calorimeter.

By this ingenious device, he was able to measure directly the heat of reaction. His results are as follows :—

For 1 grm.-equivalent of vitreous selenium—

52·2 57·2 58·2 Mean, 55·8 K.

For red precipitated selenium—

55·8 51·2 Mean, 53·4.

These results are practically identical within the limit of experimental error. They indicate that Regnault's value is far too low, a conclusion that is only confirmed by later results. The material used by Fabre was afterwards tested as to its specific gravity, and found to give as a result 4·78 for the first, and 4·79 for the second; hence the transformation was probably complete.

Fabre used an indirect method to confirm these conclusions, namely, the action of bromine in bromine water, upon selenium. For the metallic modification he found the values 431·6—432·4—421·0; mean, 429. Unfortunately, we are not told how the material was prepared.

The crystals which separate from solutions of selenides of the alkalies gave 432—434; mean, 433. Vitreous selenium prepared by rapid cooling, on a porcelain plate, from the fused state, gave 480—495·6—485·2; mean, 486·8. The difference in the two cases may be taken at about 57 K, a result which agrees fairly well with that obtained by direct measurement.

Finally, Petersen (1891), re-determined by indirect methods the heat of transformation from the amorphous to the metallic and to the red crystalline form.

For the heat of formation of the chloride Se_2Cl_2 from vitreous selenium prepared by pouring the melted element into water, he obtained values which vary in four experiments from 240° to 250° K. Thomsen's value obtained from essentially the same material was 221·5. Petersen finds in this difference ground for the assumption that there are two different soluble vitreous forms of selenium. It is much more likely that these variations are experimental, especially since Petersen has himself shown that vitreous selenium always contains more or less of the metallic modification.

From the monoclinic red crystals which separate out of carbon disulphide, Petersen finds the heat of formation of the chloride Se_2Cl_2 to be 207·5 K. From Thomsen's data, using this value, we obtain for the heat of formation of the oxide SeO_2 from the monoclinic form, 562·0 K. Deducting this from 572·5, Thomsen's result for the oxidation of amorphous selenium, we get 10·5 K as the heat of transformation of that form into the red crystalline. By a direct comparison of the results for the heat of formation of the chloride from monoclinic and vitreous selenium we find quite a different value; but they both point at least in the same direction, that the heat value in the change from liquid selenium to monoclinic red, is positive.

Metallic selenium was prepared by Petersen by heating the element to 250°, then cooling to 180°, maintaining this temperature for a long time, and then slowly cooling. So prepared, it contains about 1 per cent of soluble selenium. The value for the heat of formation of the chloride Se_2Cl_2 from this form is 200·0 K, and for the crystals from selenide solutions 199·8 K. This gives, by calculation, for the heat of formation of the oxide SeO_2 from metallic selenium 558·2 K, a value which differs by 14·3 from Thomsen's result for the amorphous form. It should be mentioned that Petersen, in quoting Thomsen's data, makes a correction of 9 K in them for the heat of solution of SeO_2, as Thomsen's results refer to reaction in solution. Summing up the results thus far obtained, we have for the heat of transformation of liquid into metallic selenium :—

Regnault (direct)	15 K
Fabre (direct)	55
,, (indirect)	57
Petersen (indirect)	14·3

For the change from the amorphous to the vitreous form we have the very doubtful value deducible from Thomsen's results, 3·5; and for the transformation from that form to the red monoclinic, 10·5.

8. *The Specific Heat of Selenium.*

Determinations of the specific heat of liquid selenium at any temperatures above 60° necessarily give uncertain values because of the danger of some of the element going over to the crystalline form. The heat set free in this transformation has so large a value that the change of even a very small quantity would utterly falsify the results. The determinations of the specific heat of the crystalline form are not open to this objection, provided the transformation into this form has been effected completely.

The data regarding the specific heat of the different modifications of selenium are to be found in the papers of Regnault (1840 and 1856), Neumann (1865), and Bettendorf and Wüllner (1868). Regnault's first determination was undertaken with some material which showed no appreciable sulphur content, but which was not tested for tellurium; nor are any particulars given as to how the material was treated before the determinations were made. The values, when compared with later results, show that he had in hand here, in all probability, the grey metallic modification. The two forms were not well differentiated at that time. Regnault made three determinations, and

found for a range of temperature from 98° to 12°, the values :—

0·08349 0·08396 0·08368 Mean, 0·08371

Sixteen years later he returned to the subject. This time he made himself familiar with the change from the vitreous to the metallic form. An analysis of the material gave Se 97·75 per cent, Te 2·25 per cent. Here again we have no information concerning the preparation of the material, but are told merely that it was metallic selenium. The results for a range from 98° to 20° are 0·07517, 0·07563, 0·07675, 0·07709; mean, 0·07616. The method used by Regnault in both of these investigations was the ordinary calorimetric one, by heating the substance to a higher temperature, dropping it into a large mass of water, noting the rise in temperature, and correcting for the alteration in this rise due to radiation, and to the cooling effect of the surrounding atmosphere.

A determination with vitreous selenium between 87° and 19° gave the results :—

0·1036 0·1026 Mean, 0·1031.

At lower temperatures the values were as follows :—

Vitreous form	−27 to +8°	0·07461
	−20 to +7°	0·07476
	Mean,	0·07468
Metallic form	−20 to +7°	0·07323
	−16 to +7°	0·07570
	Mean,	0·07446

Thus at low temperatures the specific heat appears the same whichever form we have in hand. These results show a large variation from the earlier ones of the same author; it is unfortunate that no information is given regarding the preparation of the material; there are not even sufficient data to make possible a re-calculation of the results.

In the light of his earlier values, and of the later work which we shall have to consider below, there can be little doubt that the specific heat of metallic selenium is about 0·084, a value which varies widely from the above. It is difficult to imagine that Regnault by any error used vitreous in place of metallic selenium in the later determination; on the other hand, it is possible that he was here dealing with the red crystalline form; true, the direct production of this modification from the vitreous has never been observed with certainty, but it is not in the nature of the case impossible; and there are other isolated instances on record where the assumption of such a change is at least a convenience.

The next specific heat determinations are those made by Neumann, in Göttingen, in 1865. The method used was Regnault's. His experiments were confined to the metallic form which, it is to be inferred, was prepared by heating vitreous selenium in the water-bath. As a mean of thirteen determinations, varying from 0·0847 to 0·0872, he finds the value 0·0860. Neumann used an arbitrary thermometer, but the range over which he worked was from the temperature of boiling water down to about 21°.

Finally, in 1868, Bettendorf and Wüllner published the results of their determinations. They followed essentially the same method as Regnault, simplified in certain details according to the procedure of Kopp. Their statement that Regnault prepared his material by heating the red powder obtained from selenious acid solutions finds no support in Regnault's original papers. Furthermore, their conjecture that Neumann worked with a mixture of two forms is unnecessary. It is based on the abnormally low value for the specific gravity of Neumann's material, but this is shown elsewhere to have been most probably due to experimental error.

Metallic Selenium.—Bettendorf and Wüllner prepared their material by heating amorphous selenium in an air-bath at 100° for a week. The substance was then grey in colour, and had the specific gravity 4·797. Their values are :—

0·0840, 0·0839, 0·0846, 0·0841, 0·0828, 0·0850, 0·0870, 0·0829, 0·0825; Mean, 0·0840.

The range of temperature being from 60° down to 25°.

A second specimen prepared in an entirely different way gave the same result :—The material in this case was the crystals which separate from solutions of selenides of the alkalis on standing in contact with the air. The following values were obtained: 0·0842, 0·0838, 0·0836, 0·0847, 0·0835: or in the mean, 0·08399, the range of temperature being the same as before.

Vitreous Selenium.—The material was prepared by dropping melted selenium into cold water; since vitreous selenium softens at 40° to 50° the determinations were restricted to temperatures below 38°. The results are as follows :—0·0952, 0·0958, 0·0950; mean, 0·0953, the range of temperature being from 38° to 20°. For higher temperatures, the following results were obtained :—

Temperature.	Specific heat.
53—22°	0·1104
62—20°	0·1147

There is a possibility that these large values may be due to a certain amount of the selenium having gone over to the metallic form. They could be checked by making a determination in the reverse way, *i.e.*, by introducing the cold substance into a hot bath; here, if any such change went on, the values would come out too low.

The above results are, in summary as follows :—

Vitreous Selenium.

Temperature.	Specific heat.	Observer.
87 to 19°	0·1031	Regnault II.
−25 to + 8°	0·0747	—
38 to 20°	0·0955	B. and W.
53 to 22°	0·1104	—
62 to 20°	0·1147	—

Metallic Selenium.

98 to 12°	0·0837	Regnault I.
98 to 20°	0·0762	Regnault II.
−20 to + 7°	0·0745	—
100 to 20°	0·0860	Neumann
60 to 25°	0·0840	B. and W.

Person (*Ann.*, 1849, [3], xxvii., 263), determined the specific heat of ordinary bees' wax, a substance which, like vitreous selenium, gradually softens on being warmed. His results are :—

Temperature.	Specific heat.
−21 to 3°	0·4287
6 to 26°	0·504
26 to 42°	0·82
42 to 58°	1·72

(To be continued).

"Knowledge" Diary and Scientific Handbook for 1901.—The scope of this book is principally astronomical, though it also includes a historical summary of the advance of science in the nineteenth century. Among the principal contents may be noted tables of the most important astronomical phenomena of the year, and twelve star maps showing the night-sky for every month of the year, with a full descriptive account of the visible constellations and principal stars. The calendar of notable scientific events is very complete and full of interest. The diary portion of the book allows of a whole page to a day, besides the usual pages for cash, &c.

THE ACTION OF REDUCING AGENTS UPON NITROGEN IODIDE.*

By F. D. CHATTAWAY and H. P. STEVENS.

All ordinary reducing agents when brought into contact with nitrogen iodide, suspended in water, rapidly decompose it. In these reactions the different reducing agents are invariably oxidised while hydriodic acid and ammonia are produced. The quantity of reducing agent oxidised is found in every case to be exactly double the amount equivalent to the hydriodic acid produced, using nitrogen iodide obtained by any method. The action of sodium sulphite, sulphurous acid, arsenious oxide, antimonious oxide, stannous chloride, and hydrogen sulphide has been investigated with the following results:—

Amount of reducing agent oxidised—

Na_2SO_3 H_2SO_3 As_2S_3 Sb_2O_3 $SnCl_2$ H_2S

Amount of hydriodic acid simultaneously produced—

HI HI 2HI 2HI HI HI

All the iodine contained in nitrogen iodide therefore behaves towards reducing agents like the chlorine contained in a hypochlorite, and exerts twice its normal oxidising action.

Action of Sodium Sulphite on Nitrogen Iodide.

When a solution of sodium sulphite in excess is added to nitrogen iodide suspended in water, rapid interaction ensues, and a colourless solution, somewhat acid from the presence of hydriodic acid, results.

If the sulphite be added slowly from a burette a liquid coloured brown by free iodine is obtained when the solid has entirely disappeared; the end-point of the reaction is then easily seen by the disappearance of the colour, or starch paste may be used as an indicator. The hydriodic acid produced can afterwards be estimated in one of several ways; the most convenient, and the one usually adopted, is to titrate the clear solution with standard silver nitrate, using the blue so-called "iodide of starch" as indicator (Pisani, *Annal. d. Min.*, x., 83). The actual operation is carried out as follows:—Nitrogen iodide prepared in any one of the ways previously described (Chem. News, lxxxii., p. 63), is rapidly filtered off through asbestos by the aid of a pump, and thoroughly washed with decinormal ammonia, and finally, once with water. A number of 250 c.c. flasks having been prepared, about 0·2—0·5 grm. of the moist iodide is placed in each with about 25 c.c. of water, and titrated as rapidly as possible with decinormal sodium sulphite, shaking gently the while. The estimation of hydriodic acid by silver nitrate is then carried out in the ordinary way. Light must be rigorously excluded while washing and transferring the nitrogen iodide to the flask, and during the titration until all solid particles have disappeared.

In the tables where the results are recorded the amount of reducing agent oxidised is stated in the second line, that of the hydriodic acid produced in the third, while in the fourth is the ratio between the reducing agent oxidised and the hydriodic acid produced, calculated to the third decimal place.

The Roman numerals in the first column refer to the mode in which the nitrogen iodide used was prepared. The experiments numbered I. were made with amorphous nitrogen iodide prepared by adding a decinormal solution of iodine in potassium iodide to a strong solution of ammonia; those marked II. with material prepared similarly but using a normal solution of iodine. In those numbered III. the nitrogen iodide was made by treating finely powdered iodine with a strong solution of ammonia; in those numbered IV. iodine, precipitated by diluting a saturated solution of iodine in potassium iodide, was used. In preparing the material for those numbered V. an alcoholic solution of iodine,* and for those marked VI. a solution of iodine monochloride was added to a saturated solution of ammonia. In experiments VII. and VIII. crystalline nitrogen iodide was employed, prepared respectively by adding ammonium hydroxide to a solution of potassium hypoiodite, and by heating amorphous nitrogen iodide with ammonia, and rapidly cooling. In those numbered IX. the nitrogen iodide was prepared by adding an excess of a solution of bleaching-powder to a solution of ammonium iodide.

Although in the tables one result only with each specimen of nitrogen iodide is given, this has in every case been confirmed by from 22 to 30 concordant experiments:

Number of experiment.	N/10 $\frac{Na_2SO_3}{2}$ oxidised.	N/10 HI produced.	Ratio.
	C.c.	C.c.	
I.	87·1	43·6	2 : 1·001
II.	68·2	34·1	2 : 1
III.	47·1	23·6	2 : 1·002
IV.	70·5	35·3	2 : 1·001
V.	86·2	43·2	2 : 1·002
VI.	138·2	69·1	2 : 1
VII.	60·8	30·4	2 : 1
VIII.	98·1	49·1	2 : 1·001
IX.	80·7	40·3	2 : 0·999

In order to establish beyond question this ratio between the sodium sulphite oxidised and the hydriodic acid produced, series of experiments have been made in which the latter was estimated by other methods.

In the following series, after the decomposition of sodium sulphite, the hydriodic acid was oxidised by iron-alum and sulphuric acid, and the liberated iodine distilled off and titrated by the same sulphite solution. The distillation was carried out in a special form of apparatus (Chem. News, lxxix., 85), in which only ground glass joints are employed, and to prevent bumping, a very slow stream of carbon dioxide is led in by a capillary tube to the bottom of the boiling liquid:—

Number of expt.	N/10 $\frac{Na_2SO_3}{2}$ oxidised by nitrogen iodide used.	N/10 $\frac{Na_2SO_3}{2}$ oxidised by iodine liberated from hydriodic acid produced.	Ratio.
	C.c.	C.c.	
I.	46·0	23·0	2 : 1
II.	42·1	21 1	2 : 1·002
III.	52·7	26·3	2 : 0·998
IV.	65·6	32·7	2 : 0·997
V.	45·0	22·5	2 : 1
VI.	48·6	24·3	2 : 1

Exactly similar results were obtained when the hydriodic acid formed was estimated by adding an excess of silver nitrate, and then determining the excess by a standard solution of potassium thiocyanate.

In connection with the action of reducing agents a number of experiments were made to show the necessity for the exclusion even of the diffused light of a laboratory when working with nitrogen iodide. Some amorphous nitrogen iodide prepared by adding a solution of iodine monochloride to ammonia was taken, and carefully washed with decinormal ammonia. Approximately equal quantities were then placed in four flasks; that in flask A was titrated immediately with sodium sulphite; that in flask B was exposed to the diffused light of the laboratory on a dull winter afternoon for five minutes, and then titrated; that in C was similarly exposed for ten minutes; that in D for twenty minutes. The hydriodic acid formed in each case was afterwards estimated by silver nitrate,

* From the *American Chemical Journal*, xxiii., No. 5.

* In these cases a small residue of iodoform was left in the flask after titration.

and the ratio calculated between this and the sulphite oxidised.

	$N/10 \frac{Na_2SO_3}{2}$ oxidised.	N/10 HI present.	Ratio.
	C.c.	C.c.	
A	74·8	37·4	2 : 1
B	71·5	39·2	2 : 1·100
C	65	38·2	2 : 1·17
D	73·2	49·1	2 : 1·34

It is seen that the ratio diminishes as the time of exposure increases. This is due to a decomposition of some of the nitrogen iodide into nitrogen and hydriodic acid, a change which occurs whenever the substance is exposed to light.

A solution of sulphurous acid behaves toward nitrogen iodide as sodium sulphite does; a further action, however, accompanies this, similar to the one occurring when nitrogen iodide is exposed to light, whereby a small portion breaks up into nitrogen and hydriodic acid. This latter, as it is estimated, with that produced by the reducing agent, causes the ratio to appear too low. If, however, the amount due to the reaction with the sulphurous acid be calculated from the ammonia formed, as can easily be done when the composition of the substance is known, the quantity of sulphurous acid oxidised is found to be exactly double that equivalent to the hydriodic acid produced.

(To be continued).

CORRESPONDENCE.

MARSH'S TEST FOR ARSENIC.

To the Editor of the Chemical News.

Sir,—As considerable difficulty has been experienced when testing by Marsh's test for arsenic in the presence of sulphites, I have had occasion to thoroughly investigate the influence of these compounds upon Marsh's test, and after successfully employing for the last few weeks a filter-paper moistened with a solution of lead acetate in the first part of the chloride of calcium tube, as suggested by Mr. Estcourt (Chem. News, lxxxii., p. 295), I am happy to confirm the value of this addition to the Marsh's test for counteracting the effect of the above-mentioned sulphites.

I take the liberty of expressing the opinion (judging from the reports as published in many of the papers as to the presence of arsenic in beer and other materials) that in many instances the results obtained are based upon an erroneous interpretation of the deposits in the tube, which has been contaminated by the above-mentioned sulphites. In many instances I have found that, although the deposit in the tube very closely resembled that of arsenic, on further investigation it was found not to be so, but to consist principally of sulphur compounds.

In my own opinion no time should be lost in putting the method for the detection of arsenic on a thoroughly reliable basis, as the present unsatisfactory conditions have undoubtedly in many instances been the cause of considerable unrest and suspicion in many minds.—I am, &c.,

A. E. Berry.

The Laboratory,
A. Boake, Roberts, and Co., Ltd.,
London, Dec. 24, 1900.

DETECTION OF ARSENIC.

To the Editor of the Chemical News.

Sir,—For microscopical examinations of arsenical sublimates I use a thin sheet of mica in place of porcelain; according to the quantity present, the deposit appears as a white film or cloud, more or less distinct, and can be mounted as an ordinary transparent object, and is admirably adapted for viewing with polarised light, liquid reagents, solubility, &c.

The mica, with the deposit, is cut the size of an ordinary glass slip, and held in position by strips of gummed paper; it thus serves as a permanent record which can be photographed and enlarged.

The strips of copper from Reinsch's test can be heated between strips of mica.

The mica is about the thickness of ordinary cover glass, and should be cleaned and free from scratches, and previously examined with the same magnifying power used, both before and after heating, and with polarised light.

Sulphur polarises well, arsenious oxide does not; compounds of sulphur and arsenic are in hand, and if any marked feature presents itself I will send account of the same.

One great advantage is that the mount lies perfectly flat on the stage, and the position of any special feature can be registered by an ordinary finder; if any doubt arises from colour, Nelson's method of illumination with pure white light should be tried.

If the deposit is dissolved, it can be transferred to an ordinary glass slip, if required, by a fine platinum wire.—I am, &c.,

Thos. T. P. Bruce Warren.

88, Earlham Grove,
Forest Gate, E.

NOTICES OF BOOKS.

The Inventors' Adviser, or Every Man's Own Patent Agent. By Reginald Haddan. Fifth Edition. London: Harrison and Sons. 1900. Pp. 458.

Patent Law is no simpler than any other law; in fact, owing to its peculiar combination of law, trade, and science, it is generally admitted to be a branch of law of rather exceptional difficulty; misapprehension therefore easily arises, and serious mistakes are often made by those not well-versed in the law; under such circumstances there can be no doubt that a convenient guide to the patent system, such as the present volume, would be of great assistance.

The main object of this book is not only to explain the Patent Law, and also the Patent Office practice, but to guide the applicant for a patent so that it may be obtained in the best possible way. Part I. deals with the commercial aspect of the Patent Law. Part II. is confined to the consideration and explanation of the legal questions in British law, which will arise in carrying out the policy outlined in the first part. Part III. contains a full synopsis of the Patent Laws of all foreign and Colonial States, with methods of patenting, fees, &c. To the above is added Part IV., containing chapters upon the nature and registration of trade marks in Great Britain, and details of the requirements for registration abroad.

The Art of Dispensing: A Treatise on the Methods and Processes involved in Compounding Medical Prescriptions. Sixth Edition. Revised and Enlarged. By Peter MacEwan, F.C.S. London, Melbourne and Sydney: *The Chemist and Druggist.* 1900. Pp. 490.

The first edition of this book was published in September, 1888, and was rapidly followed by two more editions in the same year; others quickly followed, and the fifth edition, published in 1890, has been reprinted six times. In this, the Sixth Edition, the book has been again entirely re-cast, and has been expanded from 288 pages to 490 pages,

The former style and most of the material have been retained, but at least two-thirds of the book is new; for instance, the chapters on Capsules, Tablets, Incompatibles, and New Remedies are practically new, and the extent of the revision is evident throughout, in the great increase in the number of pages.

This volume is a valuable addition to pharmaceutical literature, and should be in the hands of all dispensing chemists.

A Text-Book of Paper-making. By C. F. Cross and E. J. Bevan. Second Edition. London: E. and F. N. Spon, Limited. New York: Spon and Chamberlain. 1900.

In preparing this edition the authors have adhered strictly to the original plan and scope of the work, but have introduced a good deal of new matter. Certain sections, notably those dealing with the chemistry of cellulose and the operations of sizing, loading, and colouring, have been entirely re-written; many other chapters have also been re-arranged and revised with additions.

The book is fully illustrated and well printed, and will furnish a useful guide to the student or apprentice to the art of paper-making.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxi., No. 24, December 10, 1900.

Molecular Specific Heat of Dissociable Gaseous Compounds.—M. Ponsot.—The author discusses mathematically the subject of the molecular specific heat of dissociable gaseous compounds, and comes to the conclusions that for the extreme limit of rarefaction (1) the molecular specific heat of a gaseous compound, whether under constant volume or under constant pressure, is less than that of the mixture of the elements with which this compound is resolved by dissociation; (2) the hypothesis, $C_m - C_a = O$, may perhaps be adopted as an approximate law.

The Concentration at the Electrodes in a Solution, with regard specially to the Liberation of Hydrogen by Electrolysis of a Mixture of Copper Sulphate and Sulphurous Acid.—H. J. S. Sand.—The author made the researches described in this paper with the object of finding a formula which will express the concentration at the electrodes in the solution of a single salt or a mixture. In the case of the solution of a single salt, in which Hittorff's transport values are constant, in which the diffusion obeys Fick's law, in which the metal from the salt is uniformly deposited on the electrodes, and where there are no convection currents, this can be theoretically calculated. The author uses the formula thus obtained as the base of a method for determining the diffusion coefficient of copper sulphate.

The Spectra of Samarium and Gadolinium.—Eug. Demarçay.—The author attributes the non-agreement between his list of wave-lengths of the spectrum lines of gadolinium (comprised between $\lambda = 5000$ and $\lambda = 3500$), as given by himself and by Exner, as due to the impurity of the materials used by M. Exner. He believes his own samarium to have but mere traces of gadolinium left in it, and his gadolinium the merest trace of samarium. The line spectrum of samarium is very ill-defined, and the use of the absorption spectrum, discovered by Lecoq de Boisbaudran, is better, or, better still, though more difficult in practice, is Crookes's phosphorescent spectrum. The material which furnished the test given in the paper contained, in its visible spectrum, mere traces of the lines of λ, $\Sigma - Z\varepsilon$ and Gd. $\Sigma - Z\varepsilon$ is especially difficult to eliminate. Its spectrum is very sensitive, and this body is, of all the rare earths, the nearest chemically to samarium.

Action of Water-vapour and Mixtures of Hydrogen and Water-vapour on Molybdenum and its Oxides.—Marcel Guichard.—It is possible to obtain the total reduction of molybdenum oxides at a temperature below 600°. The oxidation of molybdenum by water-vapour starts at a temperature above 600° and near to 700°. By the progressive oxidation of molybdenum in water-vapour, or in mixtures of hydrogen and water-vapour, the only anhydrous oxides which are obtained are the dioxide MnO_2 and the trioxide MoO_3. Towards 800° metallic molybdenum can be obtained by total reduction of these oxides by means of a mixture of hydrogen and water-vapour of total pressure equal to the atmospheric pressure, in all cases, when the tension of the aqueous vapour in the mixture is below 350 m.m.

Remarks on M. Lemoult's Paper entitled "Relations between the Chemical Constitution of Colouring-matters of Triphenylmethane and the Absorption Spectra of their Aqueous Solutions."—Charles Camichel.—In the paper mentioned above M. Lemoult announces a relation between the position of the luminous bands of the absorption spectra of these substances and their constitution. The author states that this fact was known since the researches of M. Bayrac and himself in 1896 (*Comptes Rendus*, cxxii., p. 193, &c.), and was announced in the following law:—"If weights of each substance (of the series of the indophenol derivatives) proportional to their molecular weight are dissolved in the same weight of the solvent, the different spectra obtained show a red band of invariable position." M. Lemoult's researches are therefore merely a verification of this law.

Bulletin de la Société Chimique de Paris. Series 3, Vol. xxiii., No. 14.

The Impossibility of the Primary Formation of Chlorate of Potassium by Electrolytic Means.—A. Brochet.—Already noticed.

Thermic Examination of Gallic Acid (Trioxybenzoic Acid.—G. Massol.—Crystallised commercial gallic acid contains 1 molecule of water; the heat of solution of this hydrate is $-7{\cdot}1$ cal. The author has prepared the anhydrous acid by prolonged desiccation in an oven at 120° (it is not decomposed at this temperature), and has determined its heat of solution, which is $-4{\cdot}48$ cal. The total heat of neutralisation, measured by M. Berthelot, is $+30{\cdot}07$ cal.; in spite of this somewhat high figure gallic acid is monoacid to litmus, the same as protocatechic and salicylic acids. The aqueous solution of gallic acid, treated with 1 molecule of soda, easily gives, on evaporation in vacuo, crystallised monosodic gallate in fine needles containing 3 molecules of water. This hydrate dissolves in water with great absorption of heat $-8{\cdot}40$ cal. It completely loses its 3 molecules of water at 115°; the heat of solution of the anhydrous salt is 1·01 cal. The heat of formation of the anhydrous monosodic gallate, calculated from the above results, is—

$$C_7H_6O_5 \text{ sol.} + NaOH \text{ sol.} = C_6H_5O_5Na \text{ sol.} + H_2O \text{ sol.} \ldots 20{\cdot}86 \text{ cal.}$$

a figure higher by 3·46 cal. than the heat of formation of benzoate of soda, and which shows the influence of the three phenolic oxhydriles.

Thermic Examination of Pyrogallol-carbonic Acid (Trioxybenzoic Acid).—G. Massol.—The acid used by the author for these experiments was in the form of fine, white crystalline needles, melting at 220°; they contained

1 molecule of water of crystallisation, which they lost slowly by desiccation at 110°. Its heat of solution is −6·3 cal. The total heat of neutralisation was found to be +23·65 cal., which is much lower than that of its isomer gallic acid (+30·07 cal.). The heat of formation of the anhydrous monosodic pyrogallol carbonate was found to be—

$C_7H_6O_5$ sol. + NaOH sol. = $= C_6H_5O_5Na$ sol. + H_2O sol. . . . +19·62 cal.

This heat of formation is lower than that of the monosodic gallate by 1·24 cal., and only 0·5 cal. higher than that of the monosodic salicylate.

On Citral, and its Isomeric Forms.—Ph. Barbier.—A controversial paper replying to MM. Tiemann and Kerschbaum.—Not suitable for abstraction.

Composition of Compounds of Fuchsine with Colouring-matters, Acid by Constitution.—A. Seyewetz.—Already noticed.

MISCELLANEOUS.

Analysis of White Metal.—H. Nissenson.—White metal is an alloy of lead, antimony, tin, and a small quantity of copper. For the separation and estimation of these metals, we proceed in the following manner:—1 grm. of alloy is treated with 2 to 4 grms. of tartaric acid and 12 c.c. of water; 4 c.c. of nitric acid, of 1·4 density, are added to the solution obtained. This is heated moderately, to assist complete solution. The lead is then precipitated with 4 c.c. of concentrated sulphuric acid. It is necessary to drive off the whole of the nitric acid; a little cold water is then added, the sulphate of lead allowed to settle, and weighed in the usual manner. The solution, free from lead, is made alkaline by means of caustic soda, and then treated with 50 c.c. of a cold saturated solution of sulphide of sodium. The precipitate of sulphide of copper formed is thrown on a filter, the filtrate is collected in a platinum crucible, heated to about 80°, and subjected to the action of an electric current of about 3 volts and 1·5 ampères. When the antimony is thus entirely deposited, the liquid is quickly poured into a beaker and the precipitated antimony dried. The solution is treated with 25 grms. of pure sulphate of ammonium, to transform the sulphide of sodium into sulphide of ammonium. There then only remains to electrolyse the warm liquid with the same strength of current, to estimate the tin.—*Chemiker Zeitung*, xxiii., 868.

Estimation of Phosphoric Acid by Molybdate.—J. Hannamann.—To prevent the simultaneous precipitation of the silica with the phosphoric acid by the acid molybdic solution, it is necessary to operate in a solution containing a good deal of nitric acid and nitrate of ammonium, or else the operation should be carried out in the cold. The author has observed that the precipitation takes place more rapidly at 40°, by using a molybdic solution strong in nitric acid. The operation can be completed in ten minutes, even in solutions containing a considerable quantity of iron, and the precipitate obtained, which filters easily, can be washed rapidly, and does not adhere to the sides of the glass. By gently calcining the yellow phosphomolybdate of ammonium, we can obtain a deep-blue coloured compound of constant composition, containing, according to Meinecke, 3·94495 P_2O_5. There is no loss of molybdic acid if the whole is uniformly heated and a certain temperature not surpassed. If, after calcination, the precipitate has not the characteristic deep-blue colour, it must be moistened with ammonia, dried, and calcined again. The molybdic reagent is prepared in the following manner:—100 grms. of molybdate of ammonia are dissolved in 150 c.c. of ammonia of 0·91 density, in the presence of 100 grms. of nitrate of ammonium. The solution is poured into a litre of nitric acid ($d = 1·2$), boiled, filtered into a flask of brown glass, and kept in a cool place.—*Zeitschr. landw. Vers-Wes. Oesterr.*, 1900, iii., 53.

Determination of the Value of Basic Slags.—F. W. Daffert and O. Reitmair.—The quantity of grain harvested depends generally on the proportion of phosphoric acid in the slag, the rapidity of its action is in direct proportion with the fineness of the grinding and its chemical nature. The solubility of the phosphoric acid in slightly acid liquids enables us to judge, within certain limits, of the quality and fineness of the slag. The solubility in citrate and citric acid is not a very sure method for determining the fertilising value. The author proposes, for determining the agricultural value of a slag, to depend on the solubility of the total phosphoric acid in formic acid. A good slag yields 90 per cent of its phosphoric acid to this reagent. The total phosphoric acid is determined by precipitating an aliquot part of the nitric solution of the slag by the molybdic reagent (870 c.c. of nitric acid $d = 1·3$, 200 grms. of nitrate of ammonium, 400 grms. of molybdate of ammonium, make up to 2000 c.c.) Shake for a minute, and filter after half-an-hour. For the determination of the soluble phosphoric acid, shake up 5 grms. of slag with 5 per cent formic acid for half-an-hour. The phosphoric acid is precipitated with molybdate; the precipitate, after standing for two hours, is shaken up for fifteen minutes in a graduated cylinder. The volume it occupies is noted, and its weight is arrived at by means of a factor.—*Zeitschr. landw. Vers-Wes. Oesterr.*, 1900, iii., 75.

MEETINGS FOR THE WEEK.

MONDAY, 7th.—Society of Chemical Industry, 8. "The Early Manufacture of Sulphuric and Nitric Acids," by Oscar Guttmann. "Note on the so-called 'Heat Test' for Explosives," by W. Cullen.

TUESDAY, 8th.—Royal Institution, 3. (Christmas Lectures to Young People). "On Great Chapters from the Book of Nature," by Sir Robert Stawell Ball, D.Sc., LL.D., F.R.S.

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THE CHEMICAL NEWS.

Vol. LXXXIII., No. 2146.

THE GOLD USED BY THE ANCIENT EGYPTIANS.

By J. H. GLADSTONE, D.Sc., F.R.S.

M. Berthelot has recently made a communication to the French Academy on the subject of Egyptian gold (*Comptes Rendus*, 1900, vol. cxxxi., [9], p. 461). He gives an analysis of specimens of gold leaf from mummies of the VI. and XII. Dynasties and another specimen belonging to the Persian era. I have recently had the advantage of examining gold-foil from the Royal tombs of the First Dynasty, discovered in the early part of this year (1900) by Professor Flinders Petrie; the analyses have not yet been published. I had previously examined a specimen of gold of Adu I. of the VI. Dynasty, and another from a casket of Amenhotep II. of the XVIII. Dynasty (Dendireh, Petrie, p. 61; and *Proc. of Soc. of Antiquaries of Scotland*, vol. xxx., p. 33).

I have placed the results of all these observations in the following table, adopting Berthelot's arrangement, in which all the other substances besides the gold and silver have been classified under the heading of "Organic Matter, &c."

King.	Dynasty.	Gold.	Silver.	Organic matter, &c.	Observer.
Zet..	I.	79·7	13·4	6·9	Gladstone
Mersekha ..	,,	84·2	14·3	1·5	,,
Qa..	,,	84·0	13·0	3·0	,,
Adu I.	VI.	77·9	18·0	4·1	
		81·7	16·1	2·2	,,
—	,,	92·3	3·2	4·5	Berthelot
		92·2	3·9	3·9	
—	XII.	90·5 / 90·0	4·5	5·0	,,
Amenhotep II.	XVIII.	81·1	11·4	7·5	Gladstone
		83·5	11·7	4·8	,,
Persian Era ..	—	99·8	—	—	Berthelot

The specimens analysed by me contained little, if any, copper. M. Berthelot found no other metal present in his specimens. It is evident, on comparing these figures, that there is no similarity of composition between these different specimens of gold, except that the three kings of the First Dynasty probably drew their supplies from the same source. It is evident from the case of Amenhotep II. that, down to the sixteenth century B.C., the Egyptians continued to use the native alloy, some specimens of which almost approached that which would be designated electrum.

Some of the foil is much tarnished, and this I found to be due to the formation of chloride of silver, which of course turns dark in colour when exposed to the light. As this appears as a superficial crust, we seem here to have an instance of the slow diffusion of one part of the alloy—the silver—till it reaches the outside surface, where it meets with the chlorides that exist in the sands of the desert.

It is well known that Seti I., of the XIX. Dynasty, and his son Rameses II., worked very extensive gold-mines in the Nubian desert. It is stated by Arthur Phillips that "the gold of Nubia is of a deep yellow colour and remarkably pure." This difference could not fail to be noticed by the Egyptians; and in the great Harris papyrus, containing the annals of Rameses III., about B.C. 1200, it is perfectly evident that they distinguished different qualities of gold. Mention is made of gold, pure gold, good gold, and white gold; of best gold, and gold of the second quality; of fine gold of the land, and gold of the land of Koebti, and of Kush (see "Records of the Past," vol. vi.).

ON THE SPECTRUM OF THE MORE VOLATILE GASES OF ATMOSPHERIC AIR, WHICH ARE NOT CONDENSED AT THE TEMPERATURE OF LIQUID HYDROGEN.*

(Preliminary Notice).

By Professor G. D. LIVEING, M.A., D.Sc., Professor of Chemistry, University of Cambridge, and Professor DEWAR, M.A., LL.D., Fullerian Professor of Chemistry, Royal Institution, London.

(Concluded from p. 2).

Turning to the coronal rays, our tubes emit a weak ray at about λ 5304. This is not far from the wave-length λ 5303·7 assigned by Sir N. Lockyer to the green coronal ray. It is, however, greater than that assigned by Campbell, namely, 5303·26 (*Astroph. J.*, vol. x., p. 190). Other lines observed by us near the places of coronal lines are at wave-lengths about 4687, 4570, 4358, 4323, 4232, 4220, 3985, 3800. These are all weak lines, except that at λ 4232, which is of tolerable strength, and that at λ 4220, which is rather a strong line. The wave-lengths 4323, 4232, 4220, and 3800, come very close to those assigned to coronal rays, but the others hardly come within the limits of probable error. The ray 4220 seems too strong in proportion to the others, but the strength of that at 4232 seems to accord with the strength of the corresponding ray in the corona. It will be seen that the rays we enumerate above correspond approximately to the stronger rays in Sir N. Lockyer's list (*Roy. Soc. Proc.*, vol. lxvi., p. 191). Further measures of the wave-lengths of the faint lines are needed before we can say definitely whether or no we have in our tubes a substance producing the coronal rays, or some of them.

As to the auroral rays, we have not seen any ray in the spectrum of our tubes near λ 5571·5, the green auroral ray. We have observed two weak rays at λ 4206 and λ 4198, which may possibly, one or both, represent the auroral ray λ 420. The very strong ray of argon, λ 4200·8, would make it probable that argon was the origin of this auroral ray, if the other, equally strong, argon rays in the same region of the spectrum were not absent from the aurora. Nor have we found in the spectrum of our tubes any line with the wave-length 3915, which is that of another strong auroral line. On the other hand, it seems probable that the strong auroral line λ 358 may be due to the material which gives us the very remarkable pair of lines at about the place of N of the solar spectrum, λ 3587, which are very strong in the spectrum of the negative pole, but only faint in that of the capillary part of our tubes. It may well be that the auroral discharge is analogous to that about the negative pole. We have also a fairly strong ray at λ 3700, which may be compared to the remaining strong ray observed in the aurora λ 3700. This, however, is a ray which is emitted from the capillary part of our tubes as well as from the negative pole, and is, moreover, emitted by Bath gas, and may very likely be a neon ray.

We hope to pursue the investigation of this interesting spectrum, and if possible to sort out the rays which may be ascribed to substances such as neon and those which are due to one or more other substances. The gas from Bath, even if primarily derived from the atmosphere—which is by no means sure—seems to have undergone some sifting which has affected the relative proportions of

* A Paper read before the Royal Society, December 13, 1900.

helium and neon, and a more thorough comparison of its spectrum with that of the residual atmospheric gases may probably lead to some disentanglement of the rays which originate from different materials. The arrangement of the rays in series, if that could be done, would be a step in the same direction.

We are indebted to Mr. Robert Lennox, F.C.S., for the great help he gave us in the complicated manipulation with liquid hydrogen required to fill the spectral tubes, and to Mr. J. W. Heath, F.C.S., for kind assistance.

List of Approximate Wave-lengths of the Rays, Visible and Ultra-violet, observed about the Negative Pole.

The rays of hydrogen and helium, and those attributed to neon by other observers, are indicated by the chemical symbols of those substances:—

A "b" prefixed to the number expressing the wave-length indicates that the ray is emitted by gas from the Bath spring as well as by that obtained from the atmosphere.

A "c" similarly prefixed indicates that the ray has been observed to be emitted from the capillary part of the tube as well as from about the negative pole.

A "w" indicates a weak line; "s" strong one; "d" a diffuse one; "vw" a very weak; and "vs" a very strong one.

bc	He	7281·8			5592		
		7247		b	5561		
		7174			5532		
bc	He	7065·5		vwb	5503		
vw		7058		vw	5447		
bc	Ne	7034		wb	5432		
bc	Ne	6931		vw	5417		
bc	Ne	6716		vwb	5409		
bc	He	6678·4		b	Ne 5400		
bc	Ne	6601			5372		
sc	H	6563			5360		
bc		6535			5355		
bc	Ne	6508		bc	Ne 5341 a pair		
vwbc		6446		bc	Ne 5330		
bc	Ne	6404		w	5304		
bc	Ne	6382		w	5298		
bc	Ne	6334			5234		
bc	Ne	6304		b	5222		
bc	Ne	6266			5209		
bc		6244		b	Ne 5204		
bc		6232		b	5192		
bc	Ne	6217		b	Ne 5188		
b		6183			5152		
vwbc		6176		b	Ne 5145		
bc	Ne	6163			5122		
bc	Ne	6144		b	Ne 5116		
vwb		6128		b	Ne 5080		
b	Ne	6097			5074		
b	Ne	6075		b	He 5047·8		
b	Ne	6031		sbc	5038		
b		6001			5031		
b		5991		b	He 5015·7		
wb		5987		wd	4958		
bc	Ne	5976		b	He 4922·1		
wb		5964		vw	4884		
sdb	Ne	5945		sc	H 4861·5		
w		5919		vwb	4838		
w		5914		vw	4819		
wb		5905		vwb	4811		
bc		5882		wd	4791		
bc	He	5875·9		wd	4754		
vsbe	Ne	5852·7		b	Ne 4715		
sb		5820		b	Ne 4710		
sb		5804		b	Ne 4704		
sbc		5763		w	4687		
bc		5747		w	4680		
bc		5718			4664		
bc		5689		wb	4657		
wbc		5662		w	4647		
bc		5656		wb	4640		
w		4636		s	He 3964·9		
w		4628		vw	3933		
w		4616		b?	He? 3927		
w		4589			3905		
w		4583			3900		
		4576		vsbc	He 3888·8		
w		4570		wbc	He? 3872		
		4540		bc	He 3867·6		
		4538		w	3866		
w		4526		w	3862		
w		4523		wc?	3860		
w		4518		w	3856		
w		4508		w	3842		
w		4500		w	3840		
w		4488		c	H 3836		
vs	He	4471·6		b	3830		
vw		4460		sbc	He 3819·75		
		4457		wc	He? 3806		
vw		4438		w	3800		
wb	He	4437·7		c	H 3798		
		4431			3777		
		4429		w	H 3770		
		4424			3766		
		4422			3754		
		4413			3751		
		4409		vw	3745		
		4398		w	3738		
		4392		? c	3735		
b	He	4388·1		? c	3728		
		4380		w	3722		
w		4370		w	3721·5		
vw		4365		s	3713		
w		4363			3710		
w		4358		bc	He 3705·2		
vw		4347		w	3703		
s	H	4340·7			3701		
w		4334		s c?	3694		
vw		4322		c	3686		
vw		4315		c	3683		
vw		4306		sc	3664		
w		4290			3655		
		4276			3651		
w		4270		w	3650		
w		4261			3644 a pair		
w		4258		sc	He? 3634 a pair		
		4251		vw	3628		
		4241		bc	He 3613·8		
		4234		w	3609		
		4232		bc	He? 3600		
		4220		sbc	3593		
w		4218		vs	3587·5 a pair		
w		4206			3575		
vw		4198		w	3571		
wc		4176			3569		
wb	He	4169·1		w	3561		
w		4151		w	3558		
b	He	4143·9		vwb	3548		
w		4134			3543		
b		4131		vscb	3521		
wb		4128		bc	3515		
b	He	4121		wbc	3510		
w		4112		w	3504		
sc	H	4102		bc	3500		
w		4099		bc	He? 3498		
vw		4086			3482		
w		4080			3481		
w		4063		sbc	3473		
		4047		bc	3467		
vw		4043		bc	3464		
vw		4037		bc	3460		
vsbc	He	4026·3		w	3456		
b	He?	4009		bc	3454		
w		3996		wc	3451		
vw		3985		sbc	He 3447·7		
vw		3980		w	3429		
sc	H	3970		w	3424		

sbc	3418	s	3324
vw	3417	sb	3319
w	3407	w	3315
w	3404	w	3313
b	3393	w	3311
b	3388		3310
s	3378	b He?	3297
vw	3374	vw	3254
w	3372	wb	3250
bc	3370	s	3244
	3367		3233
w	3363	? pair	3230
vw	3362		3225
	3360	s	3218
	3358		3214
b He	3354·7		3209
s	3345		3199
w	3344	sb He	3187·8
s	3335	w	3165
	3329	w	3142
	3327		

THE IODOMETRIC ESTIMATION OF ARSENIC ACID.*

By F. A. GOOCH and JULIA C. MORRIS.

THE interaction of a soluble arseniate and a soluble iodide in a suitably acidulated solution results, as is well known, in the reduction of the arsenic acid (more or less completely according to conditions of temperature and proportions of reagents and solvents) with the corresponding liberation of two atoms of iodine for every molecule of arsenic acid (H_3O_3AsO) reduced. Inasmuch, however, as the reaction of this process is reversible, it is necessary, in order that the reduction may be complete, to nullify the oxidising action of the iodine liberated. Theoretically this end may be accomplished in either of two ways, by volatilising the free iodine bodily or by destroying the oxidising power of the iodine by converting it to hydriodic acid. The former method was followed in a process devised for the estimation of arsenic acid and elaborated in this laboratory (Gooch and Browning, *Amer. Journ. of Science*, 1890, xl., 66). This method, as originally put forward, consisted in adding to the solution of the arseniate potassium iodide in excess of the amount theoretically indicated, with 10 c.m.^{3} of sulphuric acid of half strength, and so arranging the dilution that the total volume of the liquid should be about 100 c.m.^{3}, boiling until the volume decreased to 40 c.m.^{3}, bleaching by the cautious addition of sulphurous acid the trace of free iodine still held by the hydriodic acids, diluting, cooling, neutralising with acid potassium carbonate, and titrating with iodine, after adding the starch indicator. This process, depending upon the removal by volatilisation of all but the last traces of liberated iodine and the conversion of this minute residue by sulphurous acid, involves no secondary reactions of a sort likely to influence the main effect. It is exact and fairly rapid.

The method of Williamson (*Journ. Soc. Dyers and Colorists*, 1896, 86-89), brought forward more recently, depends upon the conversion of the liberated iodine to hydriodic acid. The interaction at ordinary temperatures of a suitably strong acid, hydrochloric or sulphuric acid, upon the mixture of the arseniate and iodide,, sets free iodine, and the liberated iodine is converted to hydriodic acid by the action of sodium thiosulphate, the end-point being the disappearance of the iodine colour.

According to Williamson's directions, 25 c.m.^{3} portions of the solution of the arseniate are treated with potassium iodide and mixed with an equal volume of hydrochloric acid of sp. gr. 1·16. The precaution is recommended that the strength of the solution of the arseniate shall not exceed the decinormal value, in order that the dilution consequent upon titration by the thiosulphate may not be too great, the reducing action brought about by the action of the strong acid upon the arseniate and iodide being reversible upon the dilution of liquid with water. This procedure thus limits the process to the determination of about 0·18 grm. of arsenic acid in 25 c.m.^{3} of the solution to be treated with an equal volume of hydrochloric acid of sp. gr. 1·16. Obviously, however, the process should, so far as the reduction is concerned, be applicable to larger amounts of arsenic, provided the strength of the acid is kept up proportionately. It is essential that the liquid at the end of the titration should contain approximately 10 per cent of its mass of absolute hydrochloric acid, or about one-third of its volume of the aqueous acid of sp. gr. 1·16.

The arsenic acid is measured either by the amount of standard thiosulphate required to bleach the iodine or by the amount of iodine required to re-oxidise the reduced arsenious acid, after neutralising with acid potassium carbonate. If the former alternative is followed, the end-reaction must be the disappearance of the yellow colour of the iodine, since in solutions so strongly acid it is impossible to place dependence upon the starch indicator; in using the latter alternative, the starch indicator is, of course, permissible and preferable.

In the direct titration of the iodine by thiosulphate, two sources of error present themselves as possibilities; first, the excessive liberation of iodine by the action of air upon the strongly acidulated iodide; and second, the liability of the thiosulphate (Norton, *Amer. Journ. of Science*, vii., 287), if present even in momentary or local excess during the process of titration, to break down under the action of strong acid, thus changing its capacity to convert iodine to hydriodic acid. The latter contingency should be remote in proportion to the caution used in adding the thiosulphate and in keeping the liquid well stirred; the former must of necessity vary with the acidity of the solution containing the iodide, the time of exposure to atmospheric action, and the degree of contact with the air incidental to stirring. We have thought it desirable, therefore, to see how far each of these possibilities is likely to interfere in the practical conduct of an ordinary analysis.

The effects likely to result simply from the strong acidification of the solution containing potassium iodide, and their variations for conditions of dilution representing the beginning and the end of a titration on the lines laid down, are shown in Table I. The solution of potassium iodide was diluted as indicated before the addition of the acid, and the iodine set free was titrated by thiosulphate.

The proportionate strength of acid and the time before titration are, obviously, the essential factors. The absolute amount of acid present and the stirring seem to make little difference.

As to the action of the hydrochloric acid on small amounts of the thiosulphate, we have the evidence of the experiments detailed in the table (Table II.), in which 1, 2, and 5 c.m.^{3} of nearly *n*/10 thiosulphate are exposed to the action of 25 c.m.^{3} hydrochloric acid, sp. gr. 1·16, without dilution or diluted with an equal volume of water, were titrated with nearly *n*/10 iodine. The condition of acidity when the volume of 50 c.m.^{3} contains 25 c.m.^{3} of hydrochloric acid, sp. gr. 1·16, is that of the beginning of titration of Williamson's process. In order that the effect of error due to such action upon the determination of arsenic acid may appear immediately, the thiosulphate and iodine used are expressed in terms of that acid.

These two sources of error, the one due to a liberation of iodine and the other due to decomposition of the thiosulphate, would naturally tend to overcome one another, but the completeness of such neutralisation would naturally be largely a matter of chance in the varying conditions of actual analysis. The experiments of Table III.,

* Contributions from the Kent Laboratory of Yale University. From the *American Journal of Science*, vol. x., No. 56.

TABLE I.

HCl (sp. gr. 1·16) taken.	KI taken.	Total volume.	$Na_2S_2O_3$ added at once. In terms of H_3O_3AsO.	$Na_2S_2O_3$ added after added five minutes. In terms of H_3O_3AsO.	$Na_2S_2O_3$ added after stirring five minutes. In terms of H_3O_3AsO.
C.m.³.	Grms.	C.m.³.	Grm.	Grm.	Grm.
25	2	50	0·0013	—	—
25	2	75	0·0004	—	—
25	2	50	—	0·0035	—
25	2	75	—	0·0019	—
25	2	50	—	—	0·0042
25	2	75	—	—	0·0021
50	2	100	0·0017	—	—
50	2	150	0·0004	—	—
50	2	100	—	0·0035	—
50	2	150	—	0·0019	—
50	2	100	—	—	0·0035
50	2	150	—	—	0·0014

TABLE II.

HCl (sp. gr. 1·16) taken.	Volume before titration.	KI	$Na_2S_2O_3$ nearly $n/10$. In terms of H_3O_3AsO.	Iodine to colour without dilution. In terms of H_3O_3AsO.	Error of titration without dilution. In terms of H_3O_3AsO.	Iodine to colour after diluting to 75 c.m.³. In terms of H_3O_3AsO.	Error of titration after dilution. In terms of H_3O_3AsO.
C.m.³.	C.m.³.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
25	26	1	0·0071	0·0062	−0·0009	0·0071	0·0000
25	50	1	0·0071	0·0071	0·0000	0·0071	0·0000
25*	50	1	0·0071	0·0079	+0·0008	0·0079	+0·0008
25	50	2	0·0141	0·0146	+0·0005	0·0146	+0·0005
25*	50	2	0·0141	0·0157	+0·0016	0·0157	+0·0016
25	30	5	0·0353	0·0336	−0·0017	0·0374	+0·0024
25	50	5	0·0353	0·0359	+0·0006	0·0359	+0·0006
25*	50	5	0·0353	0·0411	+0·0058	0·0411	+0·0058

* In these experiments the acid stood in contact with the thiosulphate five minutes before titration.

TABLE III.

HCl (sp. gr. 1·16).	KI.	Volume.	$Na_2S_2O_3$ nearly $n/10$ in terms of H_3O_3AsO,	Iodine in terms of H_3O_3AsO, at once.	Iodine in terms of H_3O_3AsO, after five min.	Error in terms of H_3O_3AsO.
C.m.³.	Grms.	C.m.³.	C.m.³.	Grm.	Grm.	Grm.	Grm.
25	2	50	1	0·0071	0·0057	—	−0·0014
25	2	75	1	0·0071	0·0071	—	0·0000
25	2	50	2	0·0141	0·0131	—	−0·0010
25	2	75	2	0·0141	0·0143	—	+0·0002
25	2	50	5	0·0353	0·0322	—	−0·0021
25	2	75	5	0·0353	0·0357	—	+0·0004
25	2	50	1	0·0071	—	0·0028	−0·0043
25	2	75	1	0·0071	—	0·0067	−0·0004
25	2	50	2	0·0141	—	0·0116	−0·0025
25	2	75	2	0·0141	—	0·0139	−0·0002
25	2	50	5	0·0353	—	0·0314	−0·0041
25	2	75	5	0·0353	—	0·0361	+0·0008

TABLE IV.

HCl.	KI.	Volume at beginning of titration.	Volume at end of titration.	H_5KAsO_4 in terms of H_3O_3AsO.	H_3O_3AsO found.	Error.
C.m.³.	Grms.	C.m.³.	C.m.³.	Grm.	Grm.	Grm.
25	2	50	51	0·0062	0·0085	+0·0023
25	2	50	52	0·0125	0·0156	+0·0031
25	2	50	55	0·0312	0·0350	+0·0038
25	2	50	55	0·0624	0·0666	+0·0042
25	2	50	73	0·1559	0·1588	+0·0029
25	2	50	73	0·1559	0·1587	+0·0028
25	2	50	73	0·1559	0·1591	+0·0032
25	2	50	73	0·1559	0·1595	+0·0036
25	3	50	73	0·1559	0·1595	+0·0036
25	1	50	73	0·1559	0·1581	+0·0022
25	2	50	73	0·1559	0·1581	+0·0022
25	2	50	73	0·1559	0·1588	+0·0029

TABLE V.

H_5KAsO_4 taken in terms of H_3O_3AsO.	H_3O_3AsO found by the thiosulphate.	Error.	H_3O_3AsO found by titration of H_3O_3As with iodine.	Error.
Grm.	Grm.	Grm.	Grm.	Grm.
0·1767	0·1798	+0·0031	0·1776	+0·0009
0·1767	0·1798	+0·0031	0·1777	+0·0010
0·1767	0·1795	+0·0028	0·1785	+0·0018
0·1767	0·1793	+0·0026	0·1785	+0·0018
0·1767	0·1794	+0·0027	0·1780	+0·0013
0·1767	0·1798	+0·0031	0·1785	+0·0018

TABLE VI.

Volume.	H_3O_3AsO taken.	H_3O_3AsO found.	Error.
C.m.³.	Grm.	Grm.	Grm.
35	0·1559	0·1559	0·0000
35	0·1559	0·1560	+0·0001
40	0·1559	0·1559	0·0000
65	0·1559	0·1559	0·0000
50	0·2495	0·2499	+0·0004
50	0·2557	0·2449	−0·0008
60	0·3119	0·3117	−0·0002
60	0·3119	0·3120	+0·0001
75	0·3119	0·3124	+0·0005
75	0·3119	0·3132	+0·0013
75	0·3119	0·3121	+0·0002
75	0·3119	0·3115	−0·0004
75	0·3119	0·3124	+0·0005

however, in which $n/10$ thiosulphate, to the amount of 1, 2, and 5 c.m.³ was added to the liquid, 50 c.m.³ and 75 c.m.³, containing 25 c.m.³ acid, and titrated with iodine at once, and after five minutes, were made to test the matter for the conditions of dilution at the beginning and at the end of a titration.

It is clear that, under the conditions covered by the experiments of the two preceding tables, the decomposition of the thiosulphate is likely to occur in greater or less degree, and that, when the acid of sp. gr. 1·16 is not much diluted, the products of decomposition are not oxidised by the iodine completely. The latter observation is quite in harmony with the fact that sulphur dioxide bleaches iodine in strong hydrochloric acid only slowly and incompletely. In such cases dilution favours further action of the iodine, but results obtained by titration with iodine in the acid solution diluted with an equal amount of water are unmodified by further dilution.

In the following tables (IV.) are recorded actual determinations of arsenic according to Williamson's process. To each 25 c.m.³ of the arseniate were added 1, 2, or 3 grms. of potassium iodide and 25 c.m.³ hydrochloric acid, sp. gr. 1·16. The iodine was bleached by nearly decinormal thiosulphate without addition of the starch indicator, which loses all delicacy in the presence of strong acid. The time occupied by each titration was about five minutes. The standards of the arseniate were determined by the vaporisation process (Gooch and Browning, *loc cit.*), the purity of reagents employed in that process having been proved by trying the process in the estimation of a solution of arsenic acid made by oxidising pure decinormal arsenious acid by iodine.

The range of error in these results is from +0·0023 grm. to +0·0042 grm., with a mean of +0·0031 grm.—not very different from what might be expected from the effect of the interaction of the strong hydrochloric acid and the iodide alone. The counter-effect due to the decomposition of the thiosulphate is not large, yet it is probably real, as will appear in the sequel. In the following series of determinations (V.), made with new solutions and new standards throughout, the arsenic acid was determined, first, by titrating the iodine set free by 25 c.m.³ of hydrochloric acid, sp. gr. 1·16, and 3 grms. potassium iodide, the solution having a total volume of

50 c.m.³ at beginning and of 75 c.m.³ at the end of titration, and, secondly, the arsenious acid produced in the first reaction was titrated, after being neutralised with acid potassium carbonate by iodine in the presence of the starch indicator.

The average error of the first operation is 0·0029 grm., not far from that of the previous series; the error of the second operation, the titration of the arsenious acid, amounts on the average to 0·0014 grm. In the second operation the error due to over-use of the thiosulphate by iodine set free outside the main reaction is obviously eliminated. The tetrathionate present after neutralisation with acid potassium carbonate, is unaffected by iodine, as we have found by titrating 25 c.m.³ *n*/10 iodine mixed with 25 c.m.³ hydrochloric acid, sp. gr. 1·16, by the thiosulphate, neutralising with acid potassium carbonate,* adding starch, and getting the starch blue with a single drop of *n*/10 iodine. The average error of this process, therefore, 0·0014, is probably due to the products of decomposition of the thiosulphate in the first operation.

From the foregoing experiments it is clear that an arbitrary correction of about 0·0030 grm. must be deducted from the indications of Williamson's process of direct titration by thiosulphate made with the greatest care under the conditions mentioned; and that a correction varying from one-half that amount (0·0015 grm.) to nothing (according to the amount of arsenious acid present) when the determination is made by iodine after neutralisation with acid potassium carbonate. After making these arbitrary corrections in the results of the preceding table, the individual variations fall within reasonable limits.

On the other hand, the vaporisation process, in which the arseniate is reduced by boiling with sulphuric acid and potassium iodide in the manner described (*loc. cit.*), gives indications reasonably regular and accurate without the application of an arbitrary correction. This process, moreover, may be shortened by restricting the volume at which heating begins so that the boiling need not be extended beyond five or six minutes. According to this slight modification, the solution of the arseniate is heated in an Erlenmeyer flask with potassium iodide to an amount about 0·5 grm. in excess of the amount theoretically required and 10 c.m.³ of sulphuric acid of half-strength in a total volume of between 50 c.m.³ and 75 c.m.³. The liquid is boiled till the iodine vapours are no longer visible in the flask above the liquid, the iodine colour in the still hot liquid is bleached by the cautious addition of sulphurous acid; the whole is diluted with cold water, and cooled quickly. The solution is nearly neutralised with potassium hydroxide, and the neutralisation is completed with acid potassium carbonate. The reduced acid is titrated with iodine after adding the starch indicator. By this procedure the results given in Table VI. were obtained.

Royal Institution.—On Tuesday next, January 15, Professor J. A. Ewing, F.R.S., will deliver the first of a Course of Six Lectures at the Royal Institution, on "Practical Mechanics (Experimentally Treated): First Principles and Modern Illustrations." On Thursday next, January 17, Dr. Arthur Willey will begin a Course of Two Lectures on "The Origin of Vertebrate Animals," and on Saturday (Jan. 19), Professor R. K. Douglas will deliver the first of Two Lectures on "The Government and People of China." The Friday Evening Discourse of January 16 will be delivered by Professor Dewar, his subject being "Gases at the beginning and end of the Century."

* It is worthy of note that, as we have found by experience, it is not possible to substitute an alkaline hydroxide for the carbonate in the early stages of the process of neutralisation, on account of the decomposing effect of the former reagent upon the tetrathionate. This effect is in proportion to the heating of the solution, but is never wholly absent even when ice is intermixed with the liquid and the greatest care taken to prevent a rise of temperature.

THE ACTION OF REDUCING AGENTS UPON NITROGEN IODIDE.*

By F. D. CHATTAWAY and H. P. STEVENS

(Concluded from page 10).

Action of Arsenious Oxide on Nitrogen Iodide.

When a solution of arsenious oxide is slowly added to nitrogen iodide suspended in excess of a solution of sodium bicarbonate until the particles disappear, ammonia, arsenic acid, and hydriodic acid are produced, and the amount of arsenious acid oxidised is found to be exactly double that which is equivalent to the hydriodic acid formed. The experiments were carried out much as before, the hydriodic acid, however, being estimated by making the liquid acid, adding silver nitrate in slight excess, and estimating the excess added by potassium thiocyanate.

Number of experiment.	N/10 $\frac{As_2O_3}{4}$ oxidised.	N/10 HI produced.	Ratio.
	C.c.	C.c.	
I.	42·3	21·1	2 : 0·997
II.	45·9	22·9	2 : 0·997
III.	37·9	18·9	2 : 0·997
IV.	44·5	22·3	2 : 1·002
VI.	43·8	21·9	2 : 1
VII.	33·2	16·6	2 : 1

Similar results were obtained when the hydriodic acid was estimated by determining the amount of a standard solution of potassium permanganate required to oxidise it to iodic acid.

Action of Antimonious Oxide on Nitrogen Iodide.

The action of antimonious oxide on nitrogen iodide is exactly similar to that of arsenious oxide, the compound being converted into the higher oxide, while ammonia and hydriodic acid are produced. Similarly the quantity oxidised is double the amount equivalent to the hydriodic acid formed. The experiments were carried out as with arsenious oxide, a decinormal solution of tartar emetic being used, and sodium bicarbonate added in larger excess.

Number of experiment.	N/10 $\frac{Sb_2O_3}{4}$ oxidised.	N/10 HI produced.	Ratio.
	C.c.	C.c.	
I.	31·3	15·7	2 : 1·003
II.	39·4	19·8	2 : 1·005
III.	32·6	16·4	2 : 1·006
IV.	26·1	13·1	2 : 1·003
VI.	38·2	19·1	2 : 1
VII.	34·7	17·4	2 : 1·001

Action of Stannous Chloride upon Nitrogen Iodide.

Stannous chloride, dissolved in the least possible quantity of dilute hydrochloric acid, readily reacts with nitrogen iodide, and if it be added slowly a little iodine is liberated. If the addition be continued till this liberated iodine just disappears, stannic chloride, ammonium chloride, and hydriodic acid alone are formed. The latter can be estimated by converting it into iodic acid by a solution of potassium permanganate, the ammonium being first expelled by a slight excess of caustic soda. The quantity of hydriodic acid formed is found to be half the amount equivalent to the stannous chloride oxidised.

Number of experiment.	N/10 $SnCl_2$ oxidised.	N/10 HI produced.	Ratio.
	C.c.	C.c.	
I.	32·5	16·6	2 : 1·009
II.	31·4	15·8	2 : 1·006
III.	40·2	20·1	2 : 1
IV.	30·7	15·5	2 : 1·003
VI.	30·1	15·1	2 : 1·003
VII.	27·9	14·0	2 : 1·003

* From the *American Chemical Journal*, xxiii., No. 5.

The ratio usually comes out slightly too high. This, as in the case of sulphurous acid, is due to a small quantity of the nitrogen iodide breaking down into nitrogen and hydriodic acid under the influence of the hydrochloric acid which must be present to keep the stannous chloride in solution.

Action of Hydrogen Sulphide on Nitrogen Iodide.

On a solution of hydrogen sulphide being added to nitrogen iodide suspended in water the solid particles rapidly disappear, sulphur is precipitated, and ammonia and hydriodic acid are produced as in other cases. If the solution of hydrogen sulphide be very slowly added, iodine is set free, and the end of the reaction can be recognised easily by its disappearance. The investigation of this action is complicated by the circumstance that during it a considerable portion of the nitrogen iodide decomposes into nitrogen and hydriodic acid, and thus the ratio between the hydrogen sulphide oxidised and the hydriodic acid produced appears too great if the latter is directly estimated.

The following estimations show that the ratio thus obtained is variable but approximately 2 : 1·2*. The hydriodic acid was determined by adding a small excess of silver nitrate, and estimating this excess by potassium thiocyanate.

Number of experiment.	N/10 $\frac{H_2S}{2}$ oxidised. C.c.	N/10 HI produced. C.c.	Ratio.
I.	28·4	16·7	2 : 1·18
II.	31·2	18·9	2 : 1·21
III.	27·3	16·8	2 : 1·23
IV.	33 0	19·8	2 : 1·2
VI.	31·6	19·5	2 : 1·23
VII.	35·8	22·5	2 : 1·26

As, however, the composition of nitrogen iodide has been definitely determined, the amount which actually reacts with the hydrogen sulphide, and consequently the quantity of hydriodic acid liberated, can be calculated from the ammonia formed. In the following experiments this was done, the nitrogen iodide which breaks up into nitrogen and hydriodic acid being neglected :—

Number of experiment.	N/10 $\frac{H_2S}{2}$ oxidised. C.c.	N/10 HI produced. C.c.	Ratio.
I.	30·8	15·4	2 : 1
II.	24·7	12·3	2 : 0·995
III.	32·2	16·2	2 : 1·005
IV.	40·4	20·3	2 : 1 005
VI.	26·8	13·4	2 : 1
VII.	20·9	10·5	2 : 1 003

It is seen that the action of hydrogen sulphide upon nitrogen iodide is perfectly normal, and that the amount of hydrogen sulphide oxidised is twice that equivalent to the hydriodic acid produced.

The close agreement between all the results obtained with such very different reducing agents places it beyond doubt that, when nitrogen iodide reacts with any reducing agent, the ratio between the amount of the latter oxidised and that of the hydriodic acid produced is as 2 : 1; in other words, that the iodine contained in nitrogen iodide behaves in these reactions like the chlorine contained in a hypochlorite, and exerts twice its normal oxidising action.

* Compare Bineau's (*Ann. Chim. Phys.*, [3], 1845, xv., 71), and Gladstone's (*Chim. Soc. Journ.*, 1852, iv., 34, and 1854, vii., 51), analytical results obtained by this method. They differ among themselves, and this accompanying decomposition was not observed.

AN IMPROVED METHOD FOR THE PRESERVATION OF NORMAL SODIUM HYDRATE.

By EDWIN DOWZARD, F.C.S.

The normal solution of sodium hydrate has always been a cause of trouble and annoyance to chemists; sometimes the stopper becomes so tightly cemented into the neck of the bottle, that the bottle has to be broken; then the continual opening of the bottle exposes the contents to the action of CO_2 present in the atmosphere, which of course is very undesirable.

A number of devices have been proposed to remedy these defects: the fault of a great number is that no surplus solution can be returned to the stock-bottle without some little trouble.

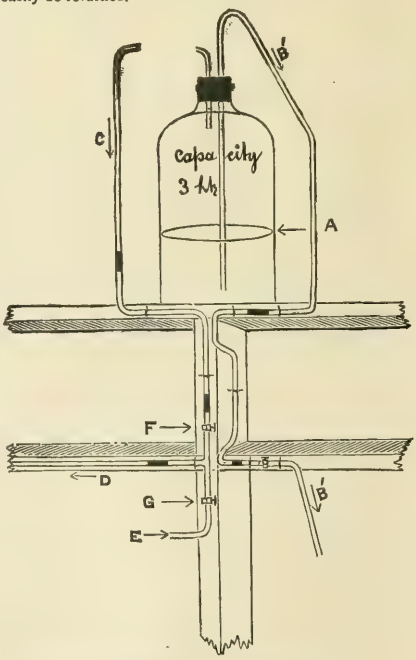
The following piece of apparatus has several advantages which recommend it:—

1. The solution is covered by a layer of white mineral oil which protects it from the action of CO_2, and also prevents evaporation.

2. The solution drawn from the bottle is always perfectly clear and free from sediment.

3. The solution is always of the same strength.

4. If too much has been withdrawn the surplus can easily be returned.



A, Layer of white mineral oil (B. P. 1898), ¼ inch thick.
B', B', Syphon with glass tap near the lower end.
C, Glass tube which can be connected to a filter-pump.
D, Filter-pump main.
E, End of filter-pump main.
F, Tap which is always kept closed except when the solution is being withdrawn or returned.

To return any unused solution to the bottle it is only necessary to start the pump, open F, close G, and place the syphon B' B' in the test-glass containing the solution; the syphon tap is now opened, when the liquid will be sucked back into the bottle.

Although this seems rather complicated, a few seconds only are required for the operation. I have had this piece of apparatus in use for about four years, and am perfectly satisfied with its action.

A NEW GENERAL METHOD FOR THE SEPARATION OF THE METALS OF THE PLATINUM GROUP.

By M. LEIDIÉ.

The methods at present in use for the extraction of platinum and iridium leave residues of which the analysis is of great interest, as they are the sole source of a certain number of the rare metals, viz., osmium, ruthenium, palladium and rhodium, besides the iridium and platinum they still contain. The following method, based on the properties of the double alkaline nitrites of these metals, enables us to effect their separation much more easily than by the dry methods of MM. H. Sainte-Claire Deville and Debray.

I. *Elimination of the Foreign Metals and Transformation of the Metals of the Platinum Group into Double Alkaline Nitrites.*

The residues of the platinum group are roasted at a dull red heat with free access of air, and are then reduced by hydrogen; the residue is washed first with water and then with dilute hydrochloric acid; finally it is again reduced by hydrogen. This preliminary operation is for the purpose of destroying the compounds in which the residual metals occur, bringing them into the metallic state and eliminating the soluble alkaline salts as well as the greater part of the iron and zinc which may have been introduced during the course of the operations.

The metallic matter is then mixed with twice its weight of fused, powdered chloride of sodium, and the mixture is heated in a current of dry chlorine to a dull red heat; the products of volatilisation, which might get lost, are condensed by means of a suitable apparatus.

In this manner all the metals are transformed into chlorides or double chlorides of more or less solubility. Both the fixed and the volatilised products are treated with water containing a little hydrochloric acid and filtered; if necessary, on account of the unattacked residue being too great, the operation is repeated. By using a quantity of water equal to 20 or 25 times the weight of the metal, but little of the chloride of lead is dissolved, and nearly the whole of the chloride of silver is removed by means of the chloride of sodium.

The solution, which must be partially neutralised with carbonate of sodium, is brought nearly to boiling point, and gradually treated with nitrite of sodium until it becomes neutral to litmus; at this moment carbonate of sodium must be further added until the precipitate no longer increases; it is then boiled for a few moments, allowed to cool, and filtered. The nitrite of sodium has precipitated the iron in the state of sesquioxide, and the gold in the metallic state; the carbonate of sodium has precipitated in the form of carbonates all the other metals, such as lead, silver, zinc, tin, bismuth, copper, &c., which were originally in the mineral or which may have been introduced accidentally during the series of operations which this latter has undergone. The metals of the platinum group have remained in solution in the state of soluble double nitrites of sodium, having the following respective formulæ:—

Nitrite of ruthenium and sodium	..	$Ru_2(NO_2)_6.4NO_2Na$
Do.	platinum	do.	.. $Pt(NO_2)_2.2NO_2Na$
Do.	palladium	do.	.. $Pd(NO_2)_2.2NO_2Na$
Do.	iridium	do.	.. $Ir_2(NO_2)_6.6NO_2Na$
Do.	rhodium	do.	.. $Rh_2(NO_2)_6\,6NO_2Na$

The osmium is present in the form of chloro-osmite, $OsCl_3.3NaCl$.

II. *Separation of the Metals of the Platinum Group.*

Osmium, Ruthenium.—The above-mentioned nitrites have the property of not being precipitated either by the alkalis or the alkaline carbonates. Their solution is treated with caustic soda and a current of chlorine is then passed through; this operation is carried out in a distilling apparatus made of glass, and of which all the parts are connected by ground joints (as for the preparation of perruthenic anhydride), and the volatile products are collected in water containing a little alcohol. The salts of osmium and of ruthenium are thus transformed into peroxides of osmium and of ruthenium, OsO_4 and RuO_4, which are volatile; gentle heat is applied towards the end of the operation to cause them to distil over with the steam; they are reduced by the alcohol to the state of osmium and ruthenium. The mixture of these two bodies is collected and the osmium separated from the ruthenium by H. Sainte-Claire Deville and Debray's method (*Annales de Chimie et de Physique* [5], vol. lvi., pp. 476, 480).

Iridium, Rhodium.—The alkaline solution, freed from osmium and ruthenium, is acidulated with hydrochloric acid and boiled; then, to re-convert the chlorides which were formed under the influence of the chlorine into nitrites, nitrite of sodium is added until the solution is neutral; it is then allowed to cool. Chloride of ammonium is then added almost to saturation point. The iridium and the rhodium are then precipitated in the form of double nitrites of ammonium: $[Ir_2(NO_2)_6.6(NO_2.NH_4)]$ and $[Rh_2(NO_2)_6.6(NO_2.NH_4)]$, which are insoluble in solutions of sal-ammoniac. The precipitate is collected after twenty-four hours and treated several times with hot aqua regia, so as to transform it into iridic chloride, $IrCl_4$, and hydrated sesquichloride of rhodium, Rh_2Cl_6. The aqua regia is driven off by evaporation, and the residue taken up with cold water saturated with chlorine. This solution is then saturated with chloride of ammonium.

The iridium is precipitated in the form of chloroiridiate of ammonium; this latter is collected, dried, mixed with its own weight of sea salt, and heated to 440—450° in a current of chlorine. The ammoniacal salt is decomposed and the iridium remains in the state of chloroiridiate of sodium, soluble in water; the rhodium which might have been entangled with it is found in the form of anhydrous sesquichloride, insoluble in water. The chloroiridiate of sodium is, by double decomposition, again transformed into chloroiridiate of ammonium. This latter, reduced at a red heat in a current of hydrogen, gives *Iridium*.

The solution from which the iridium has been precipitated is evaporated until it crystallises. The crystals of chlororhodite of ammonium, $Rh_2Cl_6\,6NH_4Cl$, are separated from those of the chloride of ammonium. The salt of rhodium is dissolved in water, transformed into the double nitrite of sodium, which is then precipitated in the form of double nitrite of ammonium (that salt of iridium, being a little more soluble, will remain in the mother liquors). This double nitrite is re-transformed by hydrochloric acid into chlororhodite of ammonium, and the latter, by reduction at a red heat in a current of hydrogen, gives *Rhodium*.

Platinum, Palladium.—The solution, freed from iridium and rhodium, now contains only platinum and palladium in the form of double nitrites; it is evaporated to dryness after the addition of hydrochloric acid to transform the nitrites into chlorides.

As the presence of chloride of sodium, which has by

this time become fairly considerable, would interfere with the complete precipitation of the platinum, the dry residue is reduced in hydrogen, and the product of the reduction washed with water, so as to leave nothing but the two metals, platinum and palladium, in the metallic form. These are dissolved in aqua regia, the excess of which is driven off by suitable evaporation, and the residue is taken up with water.

As this solution contains platinic chloride, palladic chloride, and sometimes, if the operations have been carelessly performed, *traces* of iridic chloride, and as all three are precipitable by chloride of ammonium, the second metal is transformed into palladous chloride and the third into hydrated sesquichloride of iridium, which are not precipitable. For this purpose their solution, placed in a flask which it nearly fills, is submitted to the action of a current of carbonic acid gas to drive off the air, then to a current of binoxide of nitrogen which acts as a reducing agent,* and finally to a second current of carbonic acid to drive off the binoxide of nitrogen.

The solution is then saturated with chloride of ammonium, the chloroplatinate of ammonium is collected after twenty-four hours, and crystallised two or three times in boiling water; this substance by reduction at a red heat in a current of hydrogen gives *Platinum*.

To the mother liquors mercuric cyanide is added; the palladium is precipitated in the form of palladous cyanide, $PdCy_2$. This latter is decomposed by heat, the palladium is dissolved in nitric acid, the nitrate is transformed into palladous chloride, then into nitrite of palladium and potassium; finally this latter, by the action of hydrochloric acid, is transformed into chloropalladite of potassium, which can be crystallised. This salt is then reduced at a red heat in a current of hydrogen, and the residue, cooled in a current of carbonic acid, is washed with water to remove the chloride of potassium; in this manner *Palladium* is obtained.

The metals thus prepared are in the form of a porous sponge. To obtain them in ingots they must be melted. The osmium and the ruthenium can be melted in Ducretet and Lejeune's electric furnace, in which the operation can be carried out away from contact with the air in an inert atmosphere; the others in a Sainte-Claire Deville and Debray's lime furnace, by means of a blowpipe supplied with coal-gas in the case of platinum and palladium, and with hydrogen for the iridium and rhodium.

The method I have just described has as its principal advantages, first of all the elimination, from the very commencement, of all foreign materials, the complete volatilisation of the ruthenium by which the iridium obtained by the other methods is always contaminated, and finally the fact that it does not necessitate the installation of special apparatus as in the case of the dry methods. —*Journal de Pharmacie et de Chimie*, Series 6, vol. xiii., No. 1.

Calvert's Mechanics' Almanack and Workshop Companion contains, in addition to the usual matter of an almanack, a lot of practical, technical, and industrial information for artisans and handicraftsmen, and those engaged in mechanical engineering, and building and constructive trades. There are also several pages of useful engineering diagrams.

The Gloucester Diary for 1901, published for the Gloucester Railway Carriage and Wagon Company, Limited, contains, amongst other useful information, a convenient table for immediately finding the dates of certain days of the week on which regular appointments occur; for instance, the second Tuesday, or the third Thursday in any or every month. This will be handy for finding the dates of Directors' Meetings or At Home days.

* This reducing agent is much to be preferred to those which are generally used, such as sulphurous acid or sulphydric acid. The first gives double sulphites possessing little known properties, the second sulphides which cause a loss in the returns.

THE ALLOTROPIC FORMS OF SELENIUM.*

By A. P. SAUNDERS.

(Continued from p. 8).

9. *Specific Gravity Determinations.*

THE difficulty in determining the specific gravity of selenium lies in the fact that even the smallest particles of it may contain air cavities: so that it is usually necessary, in order to get satisfactory results, that the material shall be in a state of fine powder, and that it shall be subjected to exhaustion. The easiest way to effect this is to cover the powder with some of the liquid used for filling the specific gravity bulb, place this in a desiccator, and pump out. The liquid used may be alcohol or benzene. It is to be noted that when alcohol is used, it is best, if the liquid be not pure, to pour off that part of it which has stood over the selenium, when exhausted, since it may have suffered a change of density due to the vaporisation of the more volatile component.

The determinations recorded below were all made at 25° in a specific gravity bottle of capacity 50 c.c. This was left in a bath at constant temperature for fifteen minutes. In order to test whether this was a sufficient time, the bottle was replaced in one instance, after weighing, and left in the bath for two hours longer; at the end of that time the difference in weight was only 1 m.g. The bath used was an ordinary Ostwald thermostat provided with a thermo-regulator of the usual size, but filled with toluene. This forms an instrument of a very high degree of sensitiveness, so that it was possible to keep the total variations in temperature within 0·01° for hours at a time.

It was found better to dispense with the usual stopcock where toluene was used; this was done by altering the gas-entry tube as indicated in the accompanying figure. (Fig. 3.) The tube *a* is partly filled with

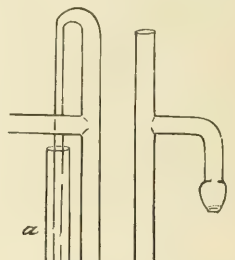


FIG. 3.

mercury, and when the desired temperature has been reached, is slipped over the end of the drawn-out tube, and held in place by a cork tied on to the neighbouring upright. The rest of the piece is arranged in the usual manner.

An attempt to use the floating method with amorphous selenium failed. The double nitrate of thallium and silver (Retgers, *Jahrb. f. Min.*, 1893 and 1896), gives a liquid of sufficient density, but selenium is at once acted upon by it.

The specific gravities of the different forms of selenium have been very often determined, and sometimes with widely varying results. The variations have been, in the main, due to the difficulty mentioned above. When the element

* From the *Journal of Physical Chemistry*, vol. iv., No. 6.

is present in fragments, these contain air cavities, which render specific gravity determinations quite hopeless.* The only method by which uniform results can certainly be obtained is to powder the material, and then exhaust for some time, best under the liquid in which the density is to be determined. This liquid should not be water, because it does not readily wet any one of the modifications of selenium; alcohol has been used in all of the more careful determinations.

Berzelius (1818), who had observed the change from the vitreous to the grey form, records the specific gravity of the former at—

4·3—4·32

and says that the transformation into the grey form causes no change of density.

The next data are those of Schaffgotsch (1848), who recognised the difficulties to be encountered, and avoided them by making the weighings in alcohol, and exhausting to get rid of the adhering air. He found at 20° for vitreous selenium, 4·276 to 4·286; for metallic selenium, prepared by heating to 250° on a sand-bath, and very slowly cooling, 4·796 to 4·805; and for the amorphous red form, 4·259 to 4·269.

Hittorf (1851), determined the density of the crystals which separate from solutions of selenides of the alkalis, and found the value 4·808; he gives no information regarding his method of determination.

In 1853, Schaffgotsch returned to the subject, and made a series of more elaborate determinations.

I. Vitreous selenium, prepared by rapid cooling, from the fused element:—

Four determinations with fragments which proved afterwards to contain air cavities, and with powder which, although boiled with water, was not rendered free from air, gave values varying by but little from 3·9. The powder, on being boiled, must certainly have gone over to the metallic form, yet Schaffgotsch records the density observed in this case as 3·9267; which goes to show how large the errors due to air cavities may be, and, particularly, the importance of choosing an appropriate liquid in which to work.

A second series, carried out with fragments which were not investigated with regard to enclosed air, gave 4·259 to 4·269.

The third series was made with air-free vitreous selenium (Schaffgotsch appears to have satisfied himself of this by inspection only), and with powder which was freed from air by repeated exhaustion under water or determined in alcohol, which, the author says, renders the use of the air-pump unnecessary. The results are very concordant, varying only from 4·276 to 4·286; or, in the mean, 4·281.

II. Metallic selenium, prepared by melting, and then very slowly cooling, gave, when powdered and determined under alcohol, values which varied in four determinations, between 4·796 and 4·805.

III. Amorphous selenium—selenium blood as Schaffgotsch calls it—gave varying results, from 4·245 to 4·275. After causing it to coagulate by heating to 50°, the results ran from 4·250 to 4·277, thus showing no difference from the powder. These last determinations were made in water. Schaffgotsch considers that, in view of the difficulties of the determination, the results are to be considered as indicating a density identical with that of vitreous selenium. The material was prepared by the addition of hydrochloric acid to a solution of selenium in sodium sulphite.

Mitscherlich (1855), studied the two red forms which separate from carbon disulphide solutions, and found their specific gravity to be 4·46 to 4·51. He seems to have taken the two forms as being identical except in crystal habit, and his density determination was possibly made with a mixture of the two. He states that it was possible by heating them to 150°, to transform them into the grey modification, whose specific gravity he found to be 4·7. The determinations were made in alcohol at 15°, and without powdering the material. The crystals which separate from selenide solutions had a density, according to Mitscherlich's results, of 4·76 to 4·79. Both of these forms—the black crystals as well as the grey material obtained from the red crystals at 150°—he therefore considered to be identical with the ordinary grey selenium whose density Schaffgotsch had found to be 4·80.

Neumann (1865), made a determination of the specific gravity of metallic selenium, and records the density of this substance "in fragments" as 4·41. This value, lying as it does so far below 4·8, suggested the possibility of there being a second form of grey metallic selenium, and most of the modern text-books describe two forms. The only further confirmation of this view is supplied by the experiments of Rammelsberg (1874), which will be found discussed below.

The next density determinations were those of Bettendorf and Wüllner (1868), who were also engaged upon the question of specific heat. The only value they give is for a sample of red amorphous selenium, which had been heated for a week in a steam-oven, and had at the end of that time a density of 4·797 at 20°. No details of the work are given, but it is obvious that they had in hand the grey form. The accuracy of the value found is due to the fact that the material, being obtained from the red powder, was already in a state of fine division, and hence no considerable error from air cavities should enter in. We come then to the paper by Rammelsberg (1874). The discrepancy between the results of Neumann's observations and those of earlier investigators seemed, to Rammelsberg, to call for a re-determination of the specific gravity of all the various forms of selenium. His determinations were made partly in alcohol, partly in water; but it does not appear that the material was powdered, nor that the air-pump was used, except perhaps in the determinations under water.

The amorphous variety obtained by the reduction of selenious acid in solution, by sulphur dioxide, gave values between 4·27 and 4·34, while melted selenium, *i.e.*, vitreous, gave 4·29 to 4·36. The crystals obtained from carbon disulphide, which are described as brownish-red and transparent, were subjected to a large number of separate determinations in alcohol; only small quantities of the crystals were used, and with very variable results, the mean values of which are given as—

4·418—4·54—4·59,

i.e., about the same as Mitscherlich had found. For the crystals which separate from selenide solutions the figures given are—

4·77—4·79—4·86.

But the most interesting values are those which Rammelsberg found for the grey metallic selenium which he prepared by heating the vitreous form to 120—150°. The product is described as insoluble in carbon disulphide, and it may therefore be assumed that it contained no considerable quantity of the vitreous form unchanged. The results for determinations made partly in alcohol and partly in water, are—

4·437—4·464—4·487—4·545—4·563—4·590,

or, in the mean, 4·514. One would have thought that the extremely large variation in these results would have aroused Rammelsberg's suspicions as to their value; but apparently not. He remarks merely that they all lie very much nearer to Neumann's value 4·4, than to Schaffgotsch's of 4·8, which is not the case. Neumann expressly states that his figure referred to selenium "in fragments," and Rammelsberg leaves the same to be inferred regarding his, whereas Schaffgotsch's determinations were made with powdered material. I made an experiment to find what difference would be observed in the density of the same material in fragments and in powder. To this end, about 2 grms. of vitreous selenium were

* The same kind of difficulty is encountered in determining the specific gravity of tellurium. (See Lenher and Morgan, *Journ. Am. Chem. Soc.*, 1900, xxii., 29).

heated for an hour at 120—150°. The product was entirely grey, and the fracture had the same colour; no trace of the red form could be observed in it. The determinations were made in alcohol at 25°. The first was made with the material broken up only enough to allow of its being brought into the specific gravity bottle. The value found was 4·55. The selenium was then taken out, dried, and powdered, replaced in the bottle, covered with alcohol, pumped out for half-an-hour, and then re-determined. The new value was 4·77. In view of these results there can be little doubt that both Rammelsberg and Neumann had in hand ordinary metallic selenium, and that the variations from the true value, 4·8, displayed by their results, are due to experimental error. This view is confirmed by the fact that Neumann found the same value for the specific heat as did Bettendorf and Wüllner, while these authors found 4·797 for the density of their material. As a further illustration of the extent to which error of this kind is possible, attention may again be called to the remark of Berzelius that the change from the vitreous to the metallic form causes no change whatever in the density (4·3). The accuracy of Rammelsberg's results with the other modifications is due to the fact that these forms having separated from solution, do not contain air cavities.

A number of density determinations were made by Petersen (1891), who prepared metallic selenium by heating the vitreous modification to 250°, then cooling to 180°, and keeping it at that temperature for a long time; finally, the material was slowly cooled. It was found to contain about 1 per cent of soluble selenium. The density determined at 17—18° was found to be 4·63 (4·62—4·64). The explanation for this very low value is to be found in the fact that the determinations, though carefully made, were carried out in water, which has always yielded unsatisfactory results with this form of the element. We have seen that Schaffgotsch obtained in this way a value as low as 4·39. The method of procedure used by Petersen was to bring the substance into the pycnometer, cover with air-free water, warm, place under the pump, and pump out until the water was caused to boil. That author drew from his result the conclusion that specific gravity cannot be taken as a criterion for the crystalline forms of selenium. But this conclusion hardly seems called for, considering that all determinations carried out with alcohol under appropriate conditions have yielded, for the metallic form, values which lie very near to 4·8.

The monoclinic red crystals obtained by extraction of amorphous selenium with carbon disulphide, yielded, by the same method as above, the values 4·44—4·47. When compared with Mitscherlich's results, which are, as before pointed out, not free from possible error, this gives as the most probable value for the density of monoclinic red selenium, a figure not differing by much from 4·47.

It will be noticed that all accurate determinations of the densities of amorphous and vitreous selenium yield results indicating a slightly lower value for the amorphous form. The following are the data on the subject:—

	Amorphous.	Vitreous.
Schaffgotsch (1848) ..	4·259—4·264	4·276—4·286
— (1853) ..	4·245—4·275	4·276—4·286
Rammelsberg ..	4·27 —4·34	4·29 —4·36

The difference is so slight as to be quite within the limits of experimental error, and the observers themselves have generally attributed it to that source; yet its constant recurrence, always in the same direction, leads to the conclusion that the two forms may really possess slightly different densities, although representing one and the same modification of the element. If this is so, the difference is due to the fact that the material exposes in one case a maximum, in the other a minimum of surface; for the amorphous form, which gives colloidal solutions with water when freshly precipitated, is in a state of extremely fine division. It is quite possible that the difference in the state of aggregation should cause a difference in density as well as in other properties of the substance. Any experiments made with selenium itself with the idea of establishiug such a difference would be rendered inconclusive by the possibility of the formation of a small amount of metallic selenium during the course of the experiment. It is, on the other hand, very easy to find analogous cases among the other elements; colloidal solutions have been prepared of gold, silver, copper, mercury, sulphur, and other elements, and all of these are obtainable in the form of impalpable powders, quite different in appearance from the compact material. Some experiments are now in progress to determine whether a measurable difference of density exists in such cases. This is not improbable if the idea suggested by Van der Waals (Ostwald, *Lehrb.*, i., 540), be correct—that there is no discontinuous change between a liquid and a vapour above it; for if there is a film of intermediate density in the case of an ordinary liquid and its vapour, it is entirely probable that solids would also have a bounding surface of lower density than the material within; equally so a viscous substance like amorphous selenium. Increasing the surface for a given weight of material would then always bring about a lowering of the density, and if the surface were made relatively large, this lowering might become apparent.

(To be continued).

CORRESPONDENCE.

DETECTION OF ARSENIC.

To the Editor of the Chemical News.

SIR,—With reference to the use of the aluminium test for arsenic, as recommended by Mr. H. G. Madan in the CHEMICAL NEWS of December 21, I would point out that this is an old and well-known test, having been first described by me, and published in the CHEMICAL NEWS of April 18, 1873. In its application care must be taken to use the purest sodic hydrate or potassic hydrate, as some specimens or "white sticks" of soda at present on the market yield distinct indications of arsenic in a blank experiment.—I am, &c.,

J. W. GATEHOUSE, F.I.C.

Grove Street, Bath.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, del'Académie des Sciences. Vol. cxxxi., No. 25, December 17, 1900.

This number contains an account of the Public Annual Meeting of the Académie.

M. MAURICE LEVY addressed the meeting, referring to the fact that during the last sixty years of this closing century science has advanced with miraculous strides. He discusses the fact as to why these discoveries should have taken place just during this period and not before.

The Jecker Prize in Chemistry is awarded to M. A. Béhal. His researches on the acetylenic carbides, the derivatives of malonic acid, chloral, chloralimide, and their derivatives are already classical. M. Béhal began in conjunction with M. Desvignes, in 1892, a series of difficult researches on asboline. These were continued with M. Choay in 1893—1895 on wood oils, in particular on the phenols which these oils contain. M. Béhal's researches on the constitution of camphor, which were re-examined by Tiemann, are those upon which the final

constitution of camphor was established. Various other investigations followed, the action of acetic acid on ethylenic and acetylenic carbides at high temperatures, the conditions for obtaining thionyle, SO, rotatory power of tartaric ethers, isomerism of tropine and pseudotropine, tantomeric forms of acetylacetic ether, distinction between crystalline and chemical molecules, commercial chloroforms, and the means of ascertaining their purity, &c. Finally, M. Béhal is the author of a "Treatise of Organic Chemistry according to Modern Theories."

The Wilde Prize was given to M. Delépine for his experimental researches on aldehydes. He especially gave attention to the ammonia compounds of the aldehydes, and to compounds of aldehydes with the alcohols, which have received the name of acetals. The derivatives of polyatomic alcohols, remarkable for their analogy with cane-sugar and the complex sugars of the same order, are specially worthy of notice. M. Delépine's researches were conducted by ordinary chemical and thermo-chemical methods. They comprise, amongst others, special determinations on formic aldehyde generated from sugars, one of the most interesting bodies of modern chemistry.

The Vaillant Prize was divided between M. Henri Gautier and M. F. Osmond. The Academy proposed the two following questions for the 1900 Vaillant Prize:—(1). Study of Metallic Alloys. (2). Precise Determinations of one or several Atomic Weights.

M. Gautier sent in papers on each of these two subjects. He proposed to investigate the fusibility of a great number of binary metallic alloys and to trace the corresponding fusibility curves. Besides this, M. Gautier investigated the atomic weight of boron by means of absolutely pure boron sulphide, which was decomposed by water. As the mean of his numerous experiments the number 11·01 was obtained.

M. Osmond's researches were on the properties of iron containing carbon. Whilst studying the different transformations of carbon he discovered a new allotropic modification of iron itself. As a result of his researches this metal is shown to possess three molecular states:—α-Iron, which is only stable at temperatures below 700°. β-Iron, which is formed between 700° and 760°, absorbing a certain amount of heat. It loses its magnetic properties, is less malleable, and a less good conductor of electricity. γ-Iron, which is formed towards 860° with a further absorption of heat, is in the same way as β-iron deprived of its magnetic properties. It is less dense than the other varieties, and a still worse conductor of electricty.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxiii., No. 15.

Oxidation of the Bibasic Acids of the Fatty Series by Acid Permanganate of Potash.—L. Perdrix.—A very long paper, not suitable for abstraction.

Action of Hexamethylenetetramine on the Ethers of the Chlor- and Brom-acetic Acids.—R. Loquin.—Hexamethylenetetramine was suspended in five times its weight of chloroform, and the theoretical quantity of chloracetate of methyl added. The mixture became heated spontaneously, while at the same time the hexamethylenetetramine was partially dissolved. On cooling the whole mass became beautifully crystalline, the crystals were analysed after draining, washing in chloroform, and desiccation in vacuo. The crystals are colourless, very soluble in water, fairly so in alcohol, and insoluble in ether, chloroform, and benzine; they melt at 141°. Analysis shows that this compound is the product of addition of a molecule of hexamethyleneamine and a molecule of chloracetate of methyl. Its formula is shown to be $C_6H_{12}N_4.CH_2ClCO_2CH_3$ or $C_6H_{12}N_4CH_2Cl.CO_2CH_3+H_2O$. Under the conditions existing it was deposited with a molecule of water of crystallisation. This reaction can be extended to the ethers of the halogen acetic acids, but experiments seem to show that it cannot be applied to the ethers of the other halogen fatty acids.

Action of Sulphurous and Sulphydric Acids on Pyridine.—G. André.—Already noticed.

Chemical Fermentation by means of Yeast in an Antiseptic Medium.—J. de Rey-Pailhade.—A quantity of brewery yeast is taken when the fermentation in a vat is just finished; it is rapidly compressed, and a little syrup of maltose added containing enough fluoride of sodium to form from 1 to 1·2 per cent of the whole. This is placed in a flask, which it should nearly fill, and closed with a cork fitted with a tap; it is kept in a cool place, and occasionally shaken. For the first two days very little carbonic acid comes off, but on the third day there is a considerable quantity formed. By watching the course of the solution of the albumenoid materials in the liquid in another flask, we observe that at the commencement, the supernatant liquid, when boiled, does not become very cloudy, while on the third day, a plentiful white coagulum is obtained. At first the still active yeast ferments but little or not at all; later on the prolonged action of the antiseptic having destroyed its vital power, it dissolves, and the primitive chemical action takes place with the evolution of carbonic acid and the probable formation of alcohol. This, however, is a point which the author has not yet confirmed. If the yeast, separated by filtration, is mixed with an aqueous solution of glucose there is no sign of fermentation; this is a proof of the death of the organism. The evolution of gas observed in contact with the antiseptic is simply a chemical phenomenon accomplished without the intervention of a living organism. The following observation appears to be of importance: the antiseptic mixture, when three days old, is rubbed up with sulphur, and almost instantaneously the evolution of carbonic acid ceases. The sulphur, acting with the yeast, gives off sulphuretted hydrogen through its combination with the *philothion* or *hydrogenase*, discovered by the author in the year 1888. This can easily be shown experimentally, by placing in two test-tubes inverted over mercury 20 c.c. each of the simple mixture, and the mixture ground up with sulphur; in the first, the evolution of gas continues for five or six days, and attains a volume of about 20 c.c.; in the latter the gas very quickly ceases to come off.

MISCELLANEOUS.

A Simple Method for the Preparation of Sulphides, Chlorides, and Bromides of the Metals from Cerite.—W. Muthmann and L. Stützel.—**I.** *Sulphides.* We start with a crystallised sulphate which is dehydrated by gentle calcination; it is then placed in a porcelain boat and heated for several hours in a combustion tube through which a current of thoroughly dry sulphuretted hydrogen is passing, raising the temperature to dull red. The colour of the product becomes darker, and in this manner we obtain perfectly pure sulphides, M_2S_3, stable in the air at the ordinary temperature, more especially if the calcination has been strong; they are only slowly attacked by boiling water, rapidly by dilute acids with the evolution of H_2S. When heated in the air these sulphides take fire; they often appear pyrophoric; in this manner oxide and sulphate are formed.

	Colour.	Density.
Cerous sulphide, Ce_2S_3 ..	Brown or black	4·9108
Sulphide of lanthanum, La_2S_3..	Yellow ..	5·020
Sulphide of neodymium, Nd_2S_3	Olive green ..	5·042
Sulphide of praseodymium, Pr_2S_3,	Bright chocolate	5·179

We have not succeeded in the preparation of Ce_2S_3, crystallising in golden-yellow flakes according to Mosander. **II.** *Chlorides and Bromides.*—We heat the sulphate, prepared as has been already described, in a current of pure thoroughly dried HCl or HBr gas; the substance becomes discoloured, and at the end of an hour a powder consisting of pure anhydrous chloride, MCl_3 (or bromide) is

obtained. Cerous chloride and bromide and chloride of lanthanum occur as white crystalline powders or masses; the chloride of neodymium is rose-coloured, that of praseodymium green. All these products greedily absorb water; they are very soluble in water and alcohol, forming a limpid solution. They are fairly fusible and slightly volatile.—*Berichte*, vol. xxxii., p. 3413.

The Sulphoxyarseniates.—L. W. McCay.– I. *Action of the Alkalis on Pentasulphide of Arsenic.*—Berzelius showed that the alkaline lyes dissolved As_2S_5, giving an arseniate and a sulpharsenate. This is not exactly true; the author has not been able to obtain a trace of precipitate of ammonio-magnesian arseniate. As a matter of fact, in this reaction (with KHO, NaHO, NH_3, or even the alkaline earths) a mixture of sulpharseniate and monosulphoxyarseniate is formed:—

$$As_2S_5+6ROH=AsS_4R_3+AsO_3SR_3+3H_2O.$$

At the same time a little disulphoxyarseniate is always likely to be formed. To prove these statements we add $SrCl_2$ to the sodic solution of As_2S_5, shake thoroughly and allow to stand for twenty-four hours. The precipitate is collected, boiled with a solution of CO_3Na_2, and the filtered liquid precipitated with alcohol; $AsO_3SNa_3+12H_2O$ is obtained. The mother-liquors of the strontium salt, treated with $BaCl_2$, deposit disulphoxyarseniate of barium, which, if treated in the same manner with CO_3Na_2, gives $AsO_2S_2Na_3+10H_2O$ on precipitating the solution with alcohol. II. *Preparation of Monosulphoxyarseniate of Sodium from a Solution of Arsenic Acid treated with Sulphydric Acid.*—Through a dilute solution of As_2O_5, a current of H_2S is passed until an abundant precipitate is formed and a quantity of finely-divided asbestos is added; the excess of H_2S is driven off by means of a strong current of air and the liquid is filtered. An excess of MgO is added to the filtered liquid to remove the unattacked As_2O_5. After filtering off the $(AsO_4)_2Mg_3$, KOH is added to precipitate the $Mg(OH)_2$, and then $Ba(OH)_2$, which precipitates the whole of the tribarytic sulphoxyarseniate in an impure state. The salt is, as before, boiled with CO_3Na_2, and the filtered liquid precipitated with alcohol until it becomes cloudy. After a few hours there is a deposit of beautiful crystals of $AsO_3SNa_3+12H_2O$ in a very pure state. The arsenious acid always remains in solution. We can obtain a solution of acid AsO_3SH_3 fairly stable in the cold, by treating the barytic salt in suspension in water with the strictly necessary quantity of dilute SO_4H_2.—*Berichte*, vol. xxxii, p. 2471.

MEETINGS FOR THE WEEK.

Monday, 14th.—Society of Arts, 8. (Cantor Lectures). "Elementary Art Education," by J. Liberty Tadd.

Tuesday, 15th.—Royal Institution, 3. "Practical Mechanics" (Experimentally treated); by Prof. J. A. Ewing, M.A., F.R.S., M.Inst.C.E.

—— Society of Arts, 8. "Cameos," by Cyril Davenport, F.S.A.

Wednesday, 16th.—Society of Arts, 8. "Photography of Natural Colours by the McDonough-Joly Process," by H. Snowden Ward.

—— Microscopical, 8. Annual Address by the President.

Thursday, 17th.—Chemical, 8. "The Preparation of Esters from other Esters of the same Acid," by T. S. Patterson and Cyril Dickinson. "Tecomin — a New Colouring-matter derived from *Bignonia tecoma*," by T. H. Lee. "A New Method for the Measurement of Ionic Velocities in Aqueous Solution," by B. D. Steele, B.Sc. "Metal-ammonia Compounds in Aqueous Solution—(II.) The Absorptive Powers of Dilute Solutions of Salts of the Alkali Metals," by H. M. Dawson and J. McCrae.

—— Royal Institution, 3. "The Origin of Vertebrate Animals," by Arthur Willey, M.A., D.Sc.

—— Society of Arts, 4.30. "Metalliferous Mining in India," by Dr. John W. Evans, LL.B., &c.

Friday, 18th.—Royal Institution, 9. "Gases at the Beginning and End of the Century," by Prof. Dewar, F.R.S., &c.

Saturday 19th.—Royal Institution, 3. "The Government and People of China," by Prof. R. K. Douglas.

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THE CHEMICAL NEWS.

Vol. LXXXIII., No. 2147.

THE ESTIMATION OF MANGANESE IN FERRO-CHROMIUM ALLOYS.

Any person undertaking the complete analysis of these alloys will find, however diligently he may search, that very few reliable methods, and only a few makeshifts, are available for the estimation of the minor elements. Processes anything like as convenient as those used for the analysis of iron and some other iron alloys do not exist. The following process may therefore be useful:—

Fuse 1 grm. of the powdered alloy with several times its weight of soda peroxide in a nickel crucible, dissolve the melt in water, boil for five or ten minutes, and filter off the peroxides of iron, manganese, and nickel. As the mixed oxides filter badly, but settle readily, they should be boiled repeatedly with water containing a little ammonium carbonate, and collected on the filter only when the yellow chromate colour is barely or not at all visible in the filtrate.

The residue and filter (asbestos) are returned to the beaker, nitric acid (1·20) and water in equal volumes are added along with as much ferrous sulphate solution as is needed to completely reduce the higher oxides of manganese and nickel.* When the precipitate has dissolved, the solution is made quite cold, oxidised with soda bismuthate, and the filtered permanganate titrated with hydrogen peroxide, according to the instructions of Reddrop and Ramage (*Journ. Chem. Soc.*, lxvii., 268).

The titrated solution is green, owing to the nickel derived from the crucible. A small excess of permanganate mixing with the green solution makes it quite colourless. The nickel of the crucible is usually quite free from manganese.

The ferro-chromiums used in steel-making are never quite free from manganese, and may contain as much as 1·5 per cent.

In order to test the above process, weighed amounts of a known iron-manganese alloy were fused along with the ferro-chromium. The amounts added in this way, and subsequently recovered in addition to that already existing in the alloy, were—

Per cent added.	Per cent found.
1·01	1·00
2·02	1·97
2·02	2·03

J. T.

* When the solution is boiled without adding any ferrous sulphate, much of the manganese is converted by the higher oxide of nickel into permanganate.

ACTION OF SUNLIGHT ON NATURAL WATERS.

By Dr. T. L. PHIPSON.

1. It has been known for a long time that when spring-water, rain-water, and river-water are exposed to sunlight, or even to diffused daylight, for a sufficient length of time in summer, the gradual development of what has been termed the "green matter" of Priestley occurs. This consists of certain mono-cellular algæ, and I have proved experimentally that they are derived (fall into the water), from the atmosphere. They are brought down very abundantly by a first fall of snow, and in rain-water. When the water is boiled and the neck of the flask closed with a good plug of cotton-wool, no development of green substance occurs after many months' exposure to sunlight; but if freely exposed to the air the microscopic plants will form in the course of a few weeks, or a few months, according to the season and temperature.

2. If a small quantity of pure crystallised cane-sugar be dissolved in the water before it is exposed to the sunlight, a different thing occurs:—

1 grm. of sugar to 300 grms. of water, exposed in a flask, the neck of which has a plug of cotton-wool to prevent germs entering from the external atmosphere, and with a summer-heat of 70° to 80° Fahrenheit, produces no green matter, but instead there form, in the course of a few days, very minute white specks, which increase in size, becoming more and more visible, and finally flocculent. Under the microscope they are found to consist of isolated mono-cellular beings like the algæ of the green matter referred to above, but these microbes are much smaller; they are extremely minute, colourless, oval cells, without any trace of green chlorophyll, and they secrete from their walls a fluid which causes them to adhere together by countless myriads, forming in the course of some months a "zoogloea," or membranous-like substance which remains *in statu quo* for more than a year.

The water filtered from it still contains sugar (after sixteen months' exposure to the sunlight).

3. It has been imagined by certain chemists that the appearance of white flocks of this kind in water containing sugar is a sign of the water being impure and unfit for drinking; but I have found that all waters, even those of exceptional purity, give rise to the same phenomenon.

My observations in this respect were made during the last two years with specimens of water of great purity from Madeira, with Thames water, and with samples of well-waters from the country.

The well-waters appear to form the white flocks rather more abundantly and rather more rapidly than the others; but the white microbe in question was developed in all.

I have also found that if the solution of sugar be boiled, and so sterilised before being added to the water, it does not prevent the occurrence of the phenomenon in question. But if the water experimented on be boiled for a quarter of an hour before the sugar is added no formation of the white microbe occurs.

This experiment proves conclusively that the germs are in the water (not in the sugar), and previous experiments have shown me that they are derived from the atmosphere.

Casa Mia, Putney, January 10, 1901.

ARSENIC IN BEER.

By E. W. T. JONES.

I beg to lay before the readers of the Chemical News the method I have been using for the detection of arsenic in beer since the beginning of December last, when the scare inundated most public analysts like myself with beer samples. I do so, notwithstanding the report of the method published by the Commission of the Manchester Brewers' Association, because, although in the main their method differs but little from mine, I personally prefer my procedure because it secures immediately on the addition of the acid the requisite conditions of Reinsch's test for the deposition of the arsenic on the copper. Before the addition of the hydrochloric acid there is no fear of arsenic being lost by the evaporation.

I also append the method I have employed with success for the *estimation* of the arsenic on the lines of Dr. Clark (*Journ. Chem. Soc.*, 1893).

Qualitative Test.

250 c.c. of the beer are evaporated in a porcelain dish over a low Fletcher burner to about 100 c.c., then 25 c.c. of pure strong hydrochloric acid are added, and into the still boiling liquid is put a piece of fine copper gauze (I prefer this to foil), about 1 inch by ½ inch, and the boiling continued for a quarter of an hour; if no darkening occurs by this time certainly less than $\frac{1}{10}$th grain per gallon of arsenic is present. If the gauze is suspiciously darkened, wash with hot distilled water, then with alcohol and dry. Roll up into a small size, and introduce into a small glass tube about three inches long, and heat the gauze with a very small flame whilst holding the tube in a horizontal position; examine any sublimate under the microscope, using a ⅛th objective. The tubing I have found very convenient is of elliptical section (I had it made originally for absorption spectroscopical work); it lies conveniently on the stage of the microscope, held on to the usual glass slips by two thin indiarubber bands, and I prepare such pieces of tube by drawing out to furnish a shoulder for the piece of gauze, and also that I may concentrate the sublimate in the narrower part.

Unmistakable octahedral or tetrahedral crystals of arsenious oxide are obtained without the least difficulty by the above procedure when $\frac{1}{10}$th grain per gallon is present.

For glucose, syrups, jams, &c., I use 50 grms., and make to 100 c.c. at once with hot distilled water, and proceed in the same way.

To prepare the copper gauze I heat a strip about an inch wide to redness in a Bunsen burner, and then remove the black oxide with nitric acid, well wash, and dry; from these beautifully bright strips I cut pieces off about a ½ inch wide for the qualitative test, and about 3½ inches long for the rolls I use for the quantitative tests.

Quantitative Test.

250 c.c. (or more) of the beer are evaporated as above in a porcelain dish to about 100 c.c., and 25 c.c. of pure strong hydrochloric acid added, then a piece of the pure bright copper gauze 1 inch × 3½ inches, in the shape of a loose roll, is put in, and the liquid is kept just on the *boil* with occasional stirring for say an hour, addition of hot distilled water being made from time to time to prevent the bulk by evaporation getting too small; considerable concentration is *advantageous* before the bulk is brought back with distilled water. The roll of gauze is now removed and washed with hot distilled water, the first washings being returned to the dish, and then another roll is put in, and the *boiling* continued.

The blackened and thoroughly washed roll is now put into a small beaker, ⅞ inch diameter and 1½ inches high, containing 5 c.c. N. sodic hydrate diluted to just cover the roll, and then 3 or 4 drops of a 10 vol. solution of peroxide of hydrogen solution added; by moving the coil up and down this solution is mixed, and on standing in the cold the gauze is gradually denuded of its black coating, and on acquiring its original colour is removed and washed into another larger beaker, these washings being reserved.

The second roll of gauze after half-an-hour's boiling in the acid beer solution is examined; if dark, is removed, washed, and treated as the first; then the first cleaned roll is introduced again, and so on, till no further deposit shows; generally the third roll shows that all the arsenic has been removed. Each roll is treated as the first, a drop or two more peroxide of hydrogen being added if required to expedite the removal of the arsenical coating.

The alkaline solution of arsenate and the washings are united and heated on the hot plate for an hour or so; then the copper precipitates, and can be filtered off. 7 c.c. of $N.H_2SO_4$ are added to the clear filtrate, and then a little pure sulphurous acid solution till the solution smells of SO_2; the solution is now boiled and concentrated till every trace of this is expelled, and to the solution, whilst hot, is added its own bulk, say 50 c.c., of saturated H_2S water; then H_2S passed through the still warm solution for a time; then it is removed to a warm place and left uncovered all night; on the following morning the As_2S_3 has collected and can be filtered off through a very small filter, and washed with water till the washings are quite free from saline matter; the As_2S_3 is now dissolved off the filter with the least possible amount of hot, very dilute ammonia water, this solution being evaporated to dryness on the hot plate in a small flat capsule (very small Petri dish covers 1¼ inches to 2 inches diam.); when cool, two or three drops of hot distilled water are added, and drop by drop *very* dilute HCl (one drop of the concentrated acid to 10 to 15 c.c. water), till the faintest acidity to litmus (this is to decompose any sulphide of ammonium); evaporate again to dryness, add 2 or 3 c.c. of H_2S water, and evaporate again to dryness; now rinse the residue with a few c.c. of distilled water, and pour off; this is easily done without detaching the sulphide; dry, boil up with CS_2 to remove S, pour off, rinse with strong alcohol, again with water, and heat on plate till *quite* dry, put under the desiccator till *dead* cold, then remove on balance with a pair of cold forceps (not with warm fingers), and weigh to the tenth of a m.grm.

Now treat the residue in the capsule with hot ammonia water; this immediately dissolves the As_2S_3, and leaves attached to the dish any trace of copper sulphide; put the solution from the dish and the rinsings into a beaker, and reserve; dry the capsule again on hot plate, and with same precautions, when cold, weigh again; the difference being As_2S_3 found.

One or two experiments should be made with pure beer, fulfilling all the conditions to see if anything is obtained from the reagents used.

To a non-arsenical beer I added at the rate of 0·1 grain per gallon of As_4O_6, and I found by the procedure I have described 0·0896, say 0·09 grain.

As a check I re-precipitated the dissolved As_2S_3 obtained, and compare with that from a solution of known strength, viz., where 1 c.c. contains 0·00018 grm. of As_4O_6, and in 250 c.c. of beer would equal 0·05 ($\frac{1}{20}$th) of a grain per gallon.

It will be observed that the actual arsenic obtained from the beer is kept and can be easily corroborated again if desired.

SMOKELESS POWDER.

By H. C. ASPINWALL.

ALTHOUGH the manufacture of smokeless powder has made enormous progress during the last few years, I am of the opinion that the question is still in the experimental stage, and that both chemists and manufacturers should continue to make great efforts to obtain the best results possible. I am well aware of the fact that the powder factories in the United States daily produce from 12,000 to 18,000 pounds of smokeless powder, the properties of which have been deemed satisfactory by the experts both of their army and their navy. It is certain that they have obtained excellent results, but the problem is one which time alone can solve: do these powders fulfil all the conditions which may arise from prolonged storage, climatic changes, &c.? As far as we know at present there is no reason to say that they do not.

Although the history of smokeless powder is probably known to many chemists, I think nevertheless that it will be of interest to recall briefly the different phases through which it has passed before reaching its present state of development.

In 1832 Braconnot discovered that on treating starch, ligneous fibres, and analogous substances with concentrated nitric acid, an extremely combustible substance could be obtained, to which he gave the name xylidine. These experiments were taken up and completed by Pelouze in 1838, and this chemist also had recourse to paper as the raw material. Some time afterwards Dumas prepared

a substance, also from paper, which he called nitramidine, and from which he proposed to make cartridges. But this substance was found to be irregular and uncertain in its action, and his researches had no practicable result up to the time when Schönbein, in 1845, announced to the world the invention of gun-cotton. In 1846 Bœttger also announced the production of gun-cotton. Eventually these two chemists became associated, finding that their discoveries were identical. At the end of 1846 Otto described a process for the manufacture of gun-cotton, and in 1847 W. Knop, in Germany, and Taylor, in England, found that gun-cotton could be prepared by means of a mixture of nitric and sulphuric acids.

At this time numerous experiments were undertaken in many countries with a view to replacing ordinary powder by this new explosive. It was, however, soon found that this was hardly possible; terrible and inexplicable explosions were of frequent occurrence, and this circumstance caused the abandonment of the experiments. Nevertheless, in Austria, Baron von Lenk was not to be frightened, and in 1862 he patented his process in England. In 1865 Abel in his turn took out a patent for an improvement which consisted essentially of reducing the gun-cotton to the form of a paste, which enabled all traces of acid and other impurities to be eliminated, and rendered it more stable.

The cutting and grinding of cellulose fibres in the apparatus then brought into use, permitted the expulsion of the free acid which they held by capillarity, and thus there was a means of removing one cause of instability. This is the method in use at the present day, and it is that which has made the extended use of gun-cotton possible.

Nitro-glycerin was discovered by Sobrero, who, by the advice of Pelouze, undertook the examination of the action of nitric acid on glycerin. It is, however, to Alfred Nobel that belongs the credit of having actually prepared the development of smokeless powder. After having invented explosive gelatin, this chemist observed that by means of a suitable solvent, nitro-glycerin and gun-cotton could be mixed in variable proportions.

In this manner he prepared a hard, horny substance, capable of being formed into grains, and of being used with perfect security as the propelling force in cannons, a substance to which he gave the name of ballistite. The most recent history of smokeless powder dates from 1886, at which time Vieille prepared B powder; in France Captain Schultz's powder appeared at almost the same time. In 1882 Reid and Johnson had introduced C. E. powder, and this had been adopted for artillery. Nobel's ballistite was patented in 1888. Since that time innumerable compositions have been proposed, the greater number of which have not given the good results expected of them.

The term gun-cotton used up to now in this article, to designate in a general manner all the varieties of nitrated cellulose, is not entirely conformable with the facts, since under this designation is generally included the most nitrated cellulose, insoluble in ether-alcohol. In what now follows the term nitro-cellulose will be employed, as better answering the conditions, and including both the soluble and insoluble varieties.

Smokeless powders known at the present time may be divided into three principal groups.

Group I.

Powders composed of nitro-cellulose, either with or without the addition of salts capable of liberating oxygen, or of inert organic substances. The group has several sub-divisions, from the point of view of the degree of nitration and the solubility of the nitro-cellulose.

a. Powder composed of detonating cotton (trinitro-cellulose containing 14·14 per cent of nitrogen, though in practice the proportion rarely exceeds 13·35 per cent). This powder is insoluble in a mixture of two parts of ether and one part of absolute alcohol, and only contains a very small proportion of soluble nitro-cellulose, generally less than 1 per cent.

b. Powders composed of a mixture of insoluble nitro-cellulose and soluble nitro-cellulose.

c. Powders composed of soluble nitro-celluloses. These three sub-divisions may be varied indefinitely by the addition of salts capable of liberating oxygen (generally alkaline nitrates), or inert organic substances, such as camphor, colouring materials, vegetable oils, mineral hydrocarbides, &c.).

Group II.

Powders containing nitro-glycerin in combination with nitro-cellulose. This group may also be sub-divided into sub-groups, from the point of view of the variety of nitro-cellulose used, and the presence or absence of oxygenated salts or inert materials.

Group III.

Powders, into the composition of which enter picrates, picric acid, or the nitro-substituted products of the aromatic carbides, in combination with one or more of the substances enumerated in groups I. and II.

Smokeless powder may also be classed according to their physical properties; that is to say, a distinction should be drawn between the powders called "bulk loading," and "compact" powders. The first have a low specific gravity, and are manufactured in such a manner that they may be changed, charge for charge, for black powder; that is to say, that the same measure which serves for the measurement of black powder can be utilised for measuring an equal volume of this class of smokeless powder, so as to give, volume for volume, approximately the same speed and the same pressure. These powders are almost exclusively used for artillery, and less often for sporting-guns using lead bullets; that is to say, in cases where it is not desirable that the speed should be higher than that given by the regular charge of black powder. The "compact" powders, on the contrary, have a high specific gravity, and the charges are made preferably by weight, seeing that the volume occupied by a full charge is not more than one-third or one-half of the volume occupied by an equivalent charge of black powder.

The smokeless powders for big guns are compact powders, the specific weight of which varies between 1·58 and 1·67, being very close to that of black powder.

It is not my intention to praise any particular class of smokeless powder. They all have their merits and their faults, and the ideal compound is yet to be found.

The manufacture of smokeless powder is a delicate operation, and to obtain satisfactory results it is necessary to observe certain indispensable conditions; the principal of which are enumerated below:—

1. The powder must be chemically stable, and when stored for a more or less prolonged period should not exhibit any signs of decomposition or disaggregation.

2. It should not undergo any change when exposed to the action of moisture, heat, cold, or climatic variations.

3. It must not be very sensitive to shock or friction.

4. It must be easy to manipulate and capable of being transported without danger.

5. The gases of combustion should not have a disagreeable odour, and should not exert any deleterious action on human beings.

6. It must be capable of being easily formed into grains of any size, and the shape of these latter should not be liable to change except within very narrow limits.

7. It must be perfectly homogeneous.

8. It should possess the highest possible ballistic power; or, in other words, it must be able to communicate the highest possible speed to the projectile, while at the same time exercising the lowest possible pressure in the gun.

It appears that nitro-cellulose, soluble or insoluble, is the material which is adapted for the manufacture of a smokeless powder fulfilling these conditions in the nearest degree. This substance enters into the composition of nearly all the smokeless powders at present known, and the ballistic results obtained are very satis-

factory, both when the nitro-cellulose is mixed with other materials and when it is used in the form of a simple colloid of nitro-cellulose.

Nitro-cellulose, in combination with nitro-glycerin, also gives very good results. It is this compound which constitutes English cordite, which is composed of 58 per cent nitro-glycerin, 37 per cent trinitro-ceilulose, and 5 per cent of vaseline.

But, on the other hand, a certain number of compounds containing nitro-glycerin, in relatively small quantity, in combination with nitro-cellulose, soluble or insoluble, have not given good results, and we are still ignorant whether this is due to the composition or the granulation, or to both these factors at once.

Nitro-glycerin, constituting a stable chemical compound, seems to be the best adapted to the preparation of smokeless powder. The action of nitric acid on glycerin,—

$$C_3H_5O_3H_3+3HNO_3=C_3H_5O_3(NO_2)_3+3H_2O,$$

produces a compound which, when purified by repeated washings, is homogeneous and stable.

Nitro-cellulose, although perfectly stable, cannot be looked upon as a definite chemical compound; it consists of a mixture of nitro-celluloses of different degrees of nitration. In view of the structure of the cellulose fibre, it has been impossible to obtain theoretical results by nitrating with a mixture of nitric and sulphuric acids.

The product known under the name of trinitro-cellulose, $C_6H_{10}O_5+3HNO_3=C_6H_7O_5(NO_2)_3+3H_2O$, yields with the nitrometer 14·14 per cent of nitrogen, while in practice we cannot obtain more than 13·35 to 13·65 per cent. The difference is due to the presence of untransformed cellulose, and perhaps also to the presence of very small quantities of lower nitrates. The soluble nitro-celluloses, whose use is very widespread in the manufacture of smokeless powders, undoubtedly consists of a mixture of nitro-celluloses of different degrees of nitration, and, for that reason, it does not seem to be as satisfactory as a definite homogeneous chemical compound.

Another disadvantage in the use of nitro-cellulose is its price, which is higher than that of nitro-glycerin.

It is not without interest to mention that Eder prepared a nitro-cellulose soluble in etherised alcohol, a substance which he called penta-nitro-cellulose,—

$$C_{12}H_5O_5(ONO_2)_5=12\cdot75 \text{ per cent nitrogen,}$$

and which appeared to be more soluble than any of the other known nitro-celluloses. However, I have quite recently prepared a soluble nitro-cellulose, showing 22·91 per cent of nitrogen with the nitrometer.—*Moniteur Scientifique*, Series 4, vol. xiv., December, 1900.

THE ALLOTROPIC FORMS OF SELENIUM.*

By A. P. SAUNDERS.

(Continued from p. 22).

Summary of Specific Gravity Results.

THE most careful determinations which have been made of the specific gravity of the various forms of selenium lead to the following results for the different modifications, at ordinary temperatures:—

Amorphous	4·26
Vitreous	4·28
Red crystalline	4·47
Metallic	4·80

Atomic Volumes.

Taking the atomic weight as 79·2, these values give the following atomic volumes:—

Amorphous	18·6
Vitreous	18·5
Red crystalline	17·7
Metallic	16·5

* From the *Journal of Physical Chemistry*, vol. iv., No. 6.

10. *Conductivity of Selenium. Action of Light.*

Beyond a vague experiment of Knox (1839), there is no information of value regarding the conductivity of selenium before 1851, when Hittorf found that the vitreous form was a very good insulator, whereas in the metallic state the element conducts electricity fairly well, and furthermore shows an unusual property, in that, unlike typically metallic substances, but like tellurium, its resistance decreases with rising temperature up to the point of fusion; at that point it suddenly increases. Hittorf used carbon plates as electrodes in his experiments.

In 1873 Willoughby Smith announced that the resistance of selenium to the passage of electricity was diminished by light. We have no details regarding the preparation of the selenium, which was in rods 5—10 c.m. long, and 1—1·5 m.m. thick. They were, plainly, of the metallic modification, as the later correspondence shows, and were sealed in glass tubes, through the ends of which platinum wires were fused for the purposes of connection. Even the light of an ordinary gas burner was found to exercise a marked influence upon the conductivity, which rose and fell according as the cell was exposed to the rays of the burner, or shaded by interposing the hand. The difference with even so feeble a source of light as this amounted to 15 to 20 per cent. "If the light be intercepted by rock salt, or by glass of various colours, the resistance varies according to the amount of light passing through the glass. To ensure that temperature was in no way affecting the experiments, one of the bars was placed in a trough of water, so that there was about an inch of water for the light to pass through, but the results were the same; and when a strong light from the ignition of a narrow band of magnesium was held about nine inches above the water, the resistance immediately fell more than two-thirds, returning to its normal condition immediately the light was extinguished."

These observations excited widespread interest, and elicited some correspondence, which will be found in the volume of *Nature* for the year 1873.

Later in the same year, Sale presented before the Royal Society the results of his researches, confirming the observations of Smith, and showing in addition that the part of the spectrum most active on selenium is just outside the red rays, at a place nearly coincident with the locus of the maximum of the heat rays. He showed further that the effect of light, on exposure, is instantaneous, but that on cutting off the light, the return to the normal resistance is not so rapid.

In 1874 Lord Rosse announced some experiments which he had made for the purpose of establishing that it was light and not heat which was the cause of the change. He compared the action of the selenium cell with that of a thermopile under similar conditions, and found no accordance between them at all. The non-luminous radiation from hot bodies had no action upon the cell, whereas the effect of candle light was not very materially diminished when allowed to pass through a plate of glass or a solution of alum.

Further confirmation of these results was supplied in 1875 by Siemens, who adds some very interesting information regarding the preparation of the cells. He found that no satisfactory results were to be obtained from material which had been transformed into the metallic modification by heating to 100° or 150°, but that by long heating to 210° or even by cooling melted selenium down to 210°, and maintaining it at that temperature for some time, "another modification," as Siemens says, is obtained, and this shows a higher degree of conductivity as well as a normal behaviour toward changes of temperature, the resistance rising as the temperature is raised. The action of light upon such material is also very much more marked, and entirely constant, the earlier cells having given variable results. Two flat spirals of platinum wire, about 1 m.m. apart, between mica plates, formed the cell, and a layer of selenium was fused over the spirals so as to fill the interspaces. This formed a very sensitive

instrument, and Siemens found that heat causes a diminution of conductivity, whereas direct sunlight increased it more than tenfold, the increase being nearly proportional to the square root of the intensity of the light. In the same year appeared a paper by Adams, bringing further confirmation of the statement that the light rays alone are active. He found that a marked effect was produced by the light of the moon, and that of the various parts of the spectrum the greenish-yellow rays were the most powerful.

Practical application of these new properties of selenium was now made in the construction of instruments for the measurement of light intensities, &c. Thus in the year 1875 Siemens described his "Electrical Photometer," Bell his "Photophone" in 1880, Bidwell his "Telephotograph" in 1881, and so on. Since the construction of these instruments had added nothing to the theory of the matter in hand, a mere mention of them will suffice.

The year 1876 is rich in memoirs. Draper and Moss undertook to determine what they call the "precise molecular state" of light sensitive selenium; but though they describe several forms of metallic selenium, which show varying behaviour toward the electric current, nothing is said of the methods of their preparation.

Later, Moss made a study of the action of mercury vapour on rods of vitreous selenium, and found that when these are allowed to stand over mercury they acquire a film of high conductivity, no doubt selenide of mercury. The same result is obtained by dipping them into mercury. Rods of the metallic modification also show increased conductivity under like circumstances. Adams, in the same year, showed that the change in resistance of selenium under light stimulus is proportional to the square root of the illuminating power. Experiments with tellurium cells indicated a distinct though very slight influence of light upon their conductivity. Adams and Day then showed that there is a change of resistance when the direction of the current passing through a selenium cell is reversed. Their method of preparation of the cell was to fuse platinum wires against the ends of a rod of vitreous selenium, and then place this in a bath of hot sand for some time. They showed, moreover, that on the whole there is a general diminution of resistance in the selenium as the battery power is increased.

Their results indicate that the conductivity of selenium cells is electrolytic. After passing the current for some time through the selenium, and then disengaging the electrodes from the battery and connecting them with the galvanometer, a current, sometimes of considerable intensity, was set up in the opposite direction, thus showing a polarisation effect. Light has an action upon this polarisation current; indeed they found that light is capable of setting up a current in such an arrangement even where no current has previously passed. The sensitiveness is different in different parts of the same piece of selenium, but in general the current is set up from the less towards the more illuminated regions. It is produced instantaneously, and falls at once to zero when the light is shut off. When the light fell upon a junction the current passed from the selenium to the platinum, through the junction.

A most important contribution to a knowledge of the subject was supplied in this year by Siemens. He endeavoured, in the first place, to find other substances showing a behaviour to light similar to that which is manifested by selenium, but in vain. Even in the case of tellurium, to which Adams had attributed this property, Siemens could find no distinct action which could not be explained as a heat effect.

In order to repeat the observation of Hittorf under better conditions, he prepared a cell with vitreous selenium and carbon electrodes. This was connected to a single Daniell cell, and plunged into a bath of paraffin maintained at 280°. A thermometer standing in the centre of the cell showed the change in temperature in the mass of the selenium, and any differences in its conductivity were read off upon a galvanometer. The results are shown in the accompanying diagram (Fig. 4).

The curve A represents the temperature of the selenium, the curve B the conductivity, and C represents a normal change of temperature for the conditions of the experiment. Time is plotted on the horizontal axis, and the values upon the vertical axis indicate temperatures for the A and C curves, and conductivities for the B curve.

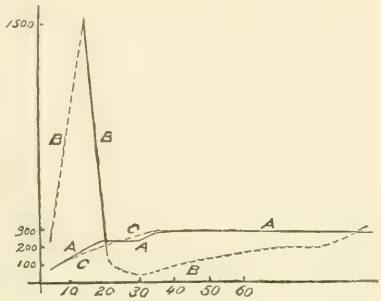


FIG. 4.

Considering first the A and C curves, we find that at about 100°, where the transformation into the metallic form would naturally begin, there is an abnormal rise in temperature. This is due to the heat of transformation. On the other hand, when we come to about 220°, there is a retardation because we have arrived at the melting-point; after complete fusion, the two curves run together again. Consider now the A and B curves. Siemens records that at 80° there was still complete non-conduction; when the thermometer had reached 162° the deflection of the galvanometer had risen to 870 scale divisions; plainly by this time a good deal of the material had gone over into the metallic (conducting) state. At 200° the deflection was 1520, but when the thermometer registered 215° it had fallen to 120 scale divisions. The thermometer, being in the middle of the mass, shows a certain lag, so that this reading of 215° doubtless corresponds to a higher temperature throughout the mass, and the fall of conductivity is due to the fact that a good deal of the selenium had already passed into a state of fusion. At about the time that complete fusion is reached, the conductivity shows a minimum, and after that, with constant temperature, it rises gradually to the end of the experiment, the temperature of the selenium remaining at about 250° to the last. The conclusion drawn from these observations by Siemens, that metallic selenium shows increasing conductivity with rising temperature, rests on insufficient ground, because the entire period between the beginning of the experiment, and the moment when the melting-point was reached was less than twenty minutes, and five minutes of this time were occupied in raising the temperature to 100°. During the remaining period there was probably a continuous change going on from the vitreous to the metallic modification, which would, of itself, bring about an increase of conductivity until the change in this direction, in the cooler parts of the cell, was balanced by a change in the opposite direction, due to fusion, in the hotter parts.

Later experiments, however, showed that the conductivity of grey selenium does increase with rising temperature.

The gradual rise in the B curve is difficult to explain except on the ground of chemical action. Shelford Badwell has shown, in a paper published somewhat later, that the peculiar behaviour of selenium cells may be due to the formation of selenides. Such a reaction might

easily go on in this case with the metallic impurities contained in the carbon electrodes; but of that more will be said later.

In another experiment, where the direct heat of a flame was used, Siemens found that the conductivity increased up to 350°, where rapid vaporisation of the selenium set in.

The remark of Siemens that, in the case of both solid and liquid selenium, the conductivity decreases with continued heating, stands in unexplained contradiction with the results of the above experiment.

If the current be passed for some time, Siemens finds a diminution of conductivity, as if polarisation had set in, opposing itself to the passage of the current.

Experiments made with metallic selenium prepared by heating the vitreous form to 150°, show that the conductivity does slowly fall when the temperature is kept constant, and also that a higher result is always obtained at a given point of temperature by cooling down to it than by heating up to it.

Siemens passed next to the use of other electrodes, namely, those of platinum and iron, having, as he says satisfied himself that solid selenium did not attack these metals. Yet it will be seen that in all the preparations he used, it was not solid selenium alone which came into contact with the metals, but liquid selenium as well, and at high temperatures. The electrodes in these experiments were either in the form of spirals, or lattice work, so as to expose a maximum surface of contact with the selenium while permitting of full illumination. On the effect of changing temperatures, the following experiment is worth transcribing.

Two cells, numbered 33 and 36, were placed in a paraffin bath, whose temperature was then rapidly raised to 200°. Both cells began to conduct at about 100°, and reached a maximum at 200°. Cell No. 33 had then a conductivity of 2720, No. 36 of 2120, in arbitrary units. The temperature was maintained for four hours.

The change with the time is shown in the table:—

	Cond.	
Time elapsed.	No. 33.	No. 36.
1 hr.	1240	940
2 hrs.	1090	820
4 hrs.	1000	800

No. 36 was then rapidly cooled, and No. 33, being slowly cooled, gave the following readings:—

Temp.	Cond.
180°	1020
150	2460
130	5730
120	8320
100	17020
80	21280

after which it diminished. On the following day it showed, at ordinary temperatures, a conductivity of 6190. Meanwhile No. 36, when suddenly cooled to room temperature, had been found to have a conductivity of 16450; after half an hour, of 14330; and on the following day 7710.

Thus these cells show a decreasing conductivity when maintained at 200°; but when cooled down, whether slowly or rapidly, the conductivity rises rapidly. This is in direct opposition to the results obtained with metallic selenium prepared in the ordinary way. The difference in preparation is that the "ordinary" form is made by heating vitreous selenium to 150°, whereas this form is produced when the same material is heated to 200°. But it must be noticed that the experiments on the other form were made with quite a different kind of cell, provided with carbon poles. The cell in these later experiments, by exposing so large a surface to the selenium, increases very much the possibility of a marked influence due to the formation of selenide at the surfaces of contact.

Bellati and Lussana (*Alt. Inst. Veneto*, 1887, [6], vi., 189, or *Ostwald's Lehrbuch*, II., ii., 422) have measured the conductivities of metallic selenides, and they find that, in general, these compounds show increasing resistance with rising temperature; *i.e.*, they conduct like metals. Furthermore, they find, in the case of copper and silver selenides, curious breaks in the curves at higher temperatures. It seems, therefore, not at all improbable that the change in selenium cells by long heating at 200°, which causes them to conduct metallically, may be explained by the formation of selenides.

Siemens finds that a cell which is only heated for a short time to 200° does not behave differently from one containing the ordinary metallic modification. In order to give to the cells the property of metallic conduction, it is necessary that the selenium should be first in the vitreous state, and that this should then be heated directly to 200°. If it has first been heated for some time at 100° and the temperature subsequently raised to 200°, the effect is either not produced at all, or to a far less degree. Nor does selenium which has been melted and cooled to 210°, and then maintained at that temperature, display any abnormal behaviour. It conducts like ordinary crystalline selenium.

Now vitreous selenium when heated to 200° is quite soft, and would be much more likely to attack metallic surfaces than the crystalline form, so that it is natural to suppose that in so far as the formation of selenide may be responsible for the behaviour of these cells, the method of heating adopted by Siemens would be most likely to produce the effect desired. By heating at 100° the mass would be almost entirely transformed at a temperature where it would be much less likely to act on the metals, and we would not expect to find any very marked reaction on heating this then to 200°.

But the second observation of Siemens recorded above, regarding the failure to prepare cells by cooling down fused selenium to 210° is, as he himself points out, in contradiction with his earlier experiments in the same direction, and it is certainly not plain why this method of preparation should not bring about as good results as the other.

From the remaining experiments reported in this paper, the following conclusions are drawn:—The observation of Adams that the conductivity of selenium cells increases for higher electromotive forces, is confirmed for such cells as have been prepared by heating vitreous selenium at once to 200°, but not for those where the transformation has been effected at lower temperatures. The effect of a continued passage of a current through a cell is the same as if a heating were thereby produced, *i. e.*, for one kind of cell it causes a rise, for the other a fall in conductivity. The change is shown not to be due to temperature. Reversing the current brings about such various phenomena that no general statement can be made about them. In some cells there is no effect at all; in others, evidence of a polarisation current.

With the cells prepared at 200°, if the heating at that temperature has been sufficiently long continued, so that the conductivity has attained a constant value, then when the temperature is lowered the conductivity shows an immediate rise. If the heating was less protracted the conductivity falls at first with falling temperature, reaches a minimum, and then rises again. The position of this minimum on the scale of temperature is dependent upon the length of the previous heating.

Selenium shows an extraordinary behaviour on change of temperature. It assumes a new conductivity value at once when the temperature is altered, and this change for rising temperature is in the direction of higher conductivity, if the selenium is of the first form (ordinary metallic), lower conductivity if it is of the second (prepared at 200°). But the new value does not remain constant For the second form, it falls after every change of temperature, no matter whether this change be up or down, and approaches a limiting value, slowly at first, then more rapidly. The

farther below the turning-point (minimum, see above) the new temperature lies, the greater is the conductivity which is at first manifested, but the more rapid also is its diminution. If the selenium has been maintained for some time at a lower temperature, so that its conductivity has fallen to a minimum, the peculiar phenomenon may be observed with the second form, that a rise of temperature brings with it at first an increase of conductivity. This is followed by a fall, and the end value is of course less than that for the lower temperature.

Cooling to -15° destroys the peculiar properties of the second form, and converts it apparently into ordinary metallic selenium.

Siemens noted the influence of the size of the surface of the electrodes on the behaviour of the cell, and also the importance of uniform contact between the selenium and the metal.

In explanation of the extraordinary behaviour of the element, he assumes that a third form is produced by continued heating at 200°, that this form is only stable at that temperature, and is at lower temperatures prevented from complete decomposition by being dissolved in, or combined with, ordinary metallic selenium. This view offers an explanation of the turning-point, beyond which the character of the conduction changes from metallic to electrolytic, and also of the fact that the cells show such a remarkable lack of uniformity of behaviour with changes of temperature.

That this assumption of a second form of metallic selenium has met with no support in my own experiments, has been shown above. Whether it will be possible to clear up all of Siemens's results by a further study of the influence of selenides upon the conductivity of selenium cells, must remain for the present an open question. Meanwhile, it is to be remembered that many of the irregularities which he noted may have had their seat in changing and irregular contact between selenium and metal; the cells were prepared with vitreous selenium, and when this goes over to the metallic form there is, as we know, a very considerable diminution in its volume: this would tend to cause rupture at any surface of contact, as well as to introduce air cavities everywhere through the material.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Extra Meeting, December 13th, 1900.

Professor Thorpe, C.B., F.R.S., President, in the Chair.

Professor H. A. Miers, D.Sc., F.R.S., delivered the Rammelsberg Memorial Lecture.

Karl Friedrich Rammelsberg was born on April 1, 1813, at Berlin, and succeeded Heinrich Rose as Professor of Inorganic Chemistry in the University of Berlin in 1874. He was also Instructor in Chemistry (1850—1883), at the Gewerbe-akademie, which became the Technische Hochschule, and was transferred to Charlottenburg in 1883; from 1883 to 1891, he was Director of the Second Chemical Institute of the University. He was twice married; in 1846, to the daughter of Oberbergrath Zincken; in 1859, to the daughter of C. G. Ehrenberg. In 1841, as Privatdocent, he started a private laboratory, in which was given the first practical chemical instruction in Berlin. He published an immense number of papers dealing with inorganic chemistry, crystallography, and mineralogy, but never himself engaged in any research work relating to organic chemistry. He was the author of numerous chemical text-books, one of which, *Grundriss der Chemie gemäss den neueren Ansichten* (1866), was the first to explain the new principles of organic chemistry. He was also the first of the old school of chemists to adopt the new system of formulæ.

Two of his books were encyclopædic works of reference: the *Handbuch der Krystallographischphysikalischen Chemie* (1855—1881), contained the crystallographic, optical, and physical constants of all crystallised compounds; the *Handbuch der Mineralchemie* (1841—1895), was an exhaustive treatise on the composition of all minerals.

He was equally eminent as Inorganic Chemist, Crystallographer, and Mineralogist. In chemistry, his work upon the halogen compounds, the phosphates, and the cyanides may be taken as samples of his researches. He prepared and studied an enormous number of bromides, of the ammonia compounds of the bromides and iodides; of bromates, iodates, and periodates; of phosphates, phosphites, and hypophosphites; our knowledge of the double cyanides is almost entirely due to him; equally laborious and important were his researches upon the sulphantimonates, hyposulphites, sulphites, nitrites, vanadates, phosphomolybdates. One of his important papers, on the Mexican amalgamation process, was communicated to this Society (1881). In crystallography, he did more than any other man to carry on the work of Mitscherlich, and investigated an immense number of isomorphous compounds; he studied the isomorphism of sulphur and selenium; he pointed out the isomorphism of vanadinite and pyromorphite, and first suggested that vanadic acid is V_2O_5; in his work upon the crystallisation of the sulphates $RSO_4,7H_2O$ from mixed solutions, he was one of the pioneers of modern physical chemistry.

In mineralogy also he contributed more than any one to our knowledge of the composition of minerals, and was practically the father of modern mineral chemistry; he published more than 300 papers on mineralogical subjects (including those on the analysis of rocks and meteorites); he first established the presence and the relationship of the ferrous and ferric iron in the group of the augites and hornblendes; he was the first to accept Tschermak's theory of the felspar group; and his laborious analyses ranged over about two-thirds of the mineral kingdom; he was strongly opposed to Penfield's views on the mutual replacement of fluorine and hydroxyl. Rammelsberg's active labours in mineral chemistry continued to the end of his long life, and at the age of 82 he published an elaborate supplement to his *Handbuch der Mineralchemie*. He died on December 28, 1899, at Gross Lichterfeld near Berlin, after a life of almost unexampled industry.

On the motion of Dr. Hugo Müller, seconded by Prof. M'Leod, a vote of thanks was passed to Prof. Miers for his Lecture.

Ordinary Meeting, December 20th, 1900.

Professor Thorpe, C.B., F.R.S., President, in the Chair.

The following certificates were read for the first time:—Messrs. Merrick William Burrows, Dunkirk, Devizes; Robert Waley Cohen, 11, Hyde Park Terrace, London, W.; Reginald Williams Ferguson, 8, Havelock Terrace, Paisley Road, Glasgow: John Lloyd Thomas Jones, United Service Club, Calcutta; James Menzies, 39, Winterbrook Road, Herne Hill, London, S.E.; Arthur W. Nunn, 313, Sydenham Road, Sydenham, S.E.; Herbert Kilburn Scott, P.O. Box 634, Rio de Janeiro, Brazil; Albert Edward Thomas, 34, South Road, Kingswood, Bristol.

Of the following papers, those marked * were read:—

*169. "*On the Union of Hydrogen and Chlorine.*" By J. W. Mellor, B.Sc.

At the suggestion of Professor H. B. Dixon the author undertook to investigate the mode in which light brings about the combination of hydrogen with chlorine. The

electrolysis of hydrochloric acid and of the solution of chlorine in this acid were first studied, as an exact knowledge of these is necessary to interpret the work of previous investigators.

Bunsen and Roscoe state that under certain conditions the gas resulting from the electrolysis of hydrochloric acid consists of a practically pure mixture of hydrogen and chlorine. The author finds, however, that under the most favourable conditions oxygen is present to the extent of 0·009 per cent.

In order to find out if the distribution of the gases in Bunsen and Roscoe's insolation vessel is effected by the absorption of hydrogen chloride, a more complete investigation was made. By plotting the respective amounts of chlorine and hydrogen chloride in the solution, it is found that two distinct and intersecting curves appear: (1). If the hydrochloric acid be less than one-fifth of normal strength, the amount of chlorine absorbed decreases as the amount of hydrogen chloride increases. The explanation is based on Jakowkin's work on the distribution ratio of chlorine between water and carbon tetrachloride, where the action of chlorine on water (in darkness) is shown to be a trimolecular one—

$$Cl_2Aq \rightleftarrows (\overset{+}{H} + \overset{-}{Cl} + HOCl)Aq.$$

The number of $\overset{+}{H}$ and $\overset{-}{Cl}$ ions is evidently increased by the addition of hydrogen chloride, and therefore in agreement with Nernst's distribution law, the number of ions derived from the chlorine is diminished. This involves a decrease in the solubility of that gas.

(2). If the strength of the solutions of hydrochloric acid be greater than one-fifth of the normal the amount of chlorine (λ) absorbed *increases* as the amount of hydrogen chloride (p) increases.

The increase is a linear function of the amount of hydrogen chloride present. $\lambda = 0{\cdot}07p + 1{\cdot}528$.

The phenomenon is probably due to the formation of a compound of hydrogen chloride with the chlorine, say HCl_3. There is no sharply defined point of transition, because the phases $\overset{+}{H}\overset{-}{Cl} + HCl_3$, &c., co-exist in the solution.

A slight contraction occurs when chlorine and hydrogen chloride gases are allowed to diffuse into each other.

*170. "*The Nitration of the Three Tolueneazophenols.*" By J. T. Hewitt and J. H. Lindfield.

The three tolueneazophenols have been nitrated by warm dilute nitric acid, and in each case the nitro-group has been found to enter the phenol nucleus in the ortho-position relatively to the hydroxyl. This agrees with the results previously obtained in the cases of oxyazobenzene and benzeneazosalicycle acid.

The following substances were described:—o-*Toluene-azo-o-nitrophenol*, m. p. 146°; the *ethyl ether*, m. p. 93°; the *acetate*, m. p. 120·5°; the *benzoate*, m. p., 132°.

m-*Toleneazo-o-nitrophenol*, m. p. 128·5°; the *ethyl ether*, m. p. 92°.

p-*Toleueneazo-o-nitrophenol*, m. p. 147°; the *ethyl ether*, m. p. 116°; the *acetate*, m. p. 94°; the *benzoate*, m. p. 129°.

The conditions under which *m*-toluneneazo-*o*-nitrophenol can be acetylated or benzoylated have not been discovered, as excess of benzoyl chloride fails to change the substance. The other acylations take place easily and normally. It is also noteworthy that difficulty is experienced in alkylating *o*-toluneneazo-*o*-nitrophenol with sodium ethoxide and ethyl bromide; the other alkylations are, however, normal.

The *ethyl ether* of *benzeneazo-o-nitrophenol* was prepared for purposes of comparison; it melts at 93°.

Discussion.

Dr. George Young inquired what evidence there was to show that acetylisation of a hydroxyazo-compound always produced an acetoxy- and not an acethydrazone derivative. It seemed curious that a change of position of a methyl group in the benzene should influence the acetylisation of the phenol side of the molecule.

Dr. Hewitt stated that though Goldschmidt claimed to have completely reduced the acetyl derivative of benzeneazo-*p*-cresol to acetanilide and *p*-cresol, MacPherson had obtained compounds by the action of benzoylphenylhydrazine on quinones which were isomeric, and not identical with the benzoyl derivatives of the azophenols. Hence it would appear that the acetyl and benzoyl derivatives of the azophenols are true oxygen ethers.

*171. "*The Bromination of the Ortho-oxyazo-compounds and its bearing on their Constitution.*" By J. T. Hewitt and H. A. Phillips.

The effect of substituting agents on numerous oxyazo-compounds of the *para*-series has been studied by one of the authors of this communication and his pupils. So far, bromination or nitration of *ortho*-oxyazo-compounds has not been examined, but it was expected that such compounds would behave as *ortho*quinone-hydrazones, and substitute in the nucleus which had been derived from the diazotised aromatic base. Thus benzeneazo-*p*-cresol was expected to give *para*- or *ortho*-bromobenzeneazo-*p*-cresol, whereas experiment has shown that when the substance is dissolved in glacial acetic acid with an excess of sodium acetate and then brominated, benzeneazo-*o*-bromo-*p*-cresol results. Ortho-oxyazo-compounds appear thus to react towards bromine as true oxyazo-compounds.

In the course of this investigation, the following compounds have been prepared and their properties examined:

Benzeneazo-o-bromo-p-cresol, m. p. 123°; *benzeneazo-o-bromo-p-cresyl acetate*, m. p. 83°; *benzeneazo-o-bromo-p-cresyl benzoate*, m. p. 110°; *o-bromobenzeneazo-p-cresol*, m. p. 116°; *o-bromobenzeneazo-p-cresyl acetate*, m. p. 85; *o-bromobenzeneazo-p-cresyl benzoate*, m. p. 106·5°; *m-bromobenzeneazo-p-cresol*, m. p. 112°; *m-bromobenzeneazo-p-cresyl acetate*, m. p. 61—62°; *m-bromobenzeneazo-p-cresyl benzoate*, m. p. 94°; *p-bromobenzeneazo-p-cresol*, m. p. 147°; *p-bromobenzeneazo-p-cresyl acetate*, m. p. 123°; *p-bromobenzeneazo-p-cresyl benzoate*, m. p. 112°.

172. "*On the use of Pyridine for Molecular Weight Determinations by the Ebullioscopic Method.*" By William Ross Innes.

The author described the precautions necessary to obtain accurate results. The constant for pyridine is 29·5. Acids, alcohols, and phenols were shown to give normal molecular weights. Pyridine therefore does not favour the association of dissolved substances.

173. "*The Influence of the Methyl Group on Ring Formation.*" By A. W. Gilbody and C. H. G. Sprankling.

The authors have prepared and analysed *p*-ethoxyphenylsuccinamic acid and the following alkyl substituted derivatives:—(1) p-*ethoxyphenylsuccinamic acid*, m. p. 166—167°; (2) *methyl*-p-*ethoxyphenylsuccinamic acid*, m. p. 149—150°; (3) as-*dimethyl*-p-*ethoxyphenylsuccinamic acid*, m. p. 160—161°; (4) trans-s-*dimethyl*-p-*ethoxyphenylsuccinamic acid*, m. p. 184—185°; (5) cis-s-*dimethyl*-p-*ethoxyphenylsuccinamic acid*, m. p. 155—156°; (6) *trimethyl*-p-*ethoxyphenylsuccinamic acid*, m. p. 128—129°; (7) *isopropyl*-p-*ethoxyphenylsuccinamic acid*, m. p. 151—152°.

Two forms of the asymmetrically substituted acids should exist according to theory, but only one has been observed during the research. The anilides of the corresponding phenylsuccinamic acids also seem to behave in a similar manner, for previous investigators have found only one acid, where two might be expected.

The scanty evidence at our disposal (Blaise, *Comptes Rendus*, 1898, cxxvi., 753) tends to show that of the two formulæ for methyl-*p*-ethoxyphenylsuccinamic acid, for example,—

$$\begin{array}{l} CH_3{\cdot}CH{\cdot}CO_2H \\ \quad\quad\quad | \\ CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4OC_2H_5 \end{array}$$

and—

$$\begin{array}{l} CH_2{\cdot}CO_2H \\ | \\ CH_3{\cdot}CH{\cdot}CO{\cdot}NH{\cdot}C_6H_4OC_2H_5, \end{array}$$

the former is the correct one.

Under the conditions employed, the lower members of the series readily yielded anhydrous sodium salts, but the salts of the trimethyl and isopropyl-"aminic" acids have not so far been obtained pure, owing to the easy formation of the ring compounds (pyrantins).

The above acids were then converted into the corresponding *p*-ethoxyphenylsuccinimide (pyrantin) derivative, and the stability of the substituted succinimide ring so produced estimated according to the well-known equation $\frac{I}{T} \cdot \frac{X}{A-x} = Ac$; the figures given being the mean of two or more determinations (compare Miolati and Longo, *Att. Accad. Lincei Rend.*, 1894, [5], iii., 515, 597; 1895, [5], iv., 351; Miolati and Lotti, 1896, [5], vi., 88; Piutti, *Ber.*, 1896, xxix., 85).

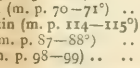
It was necessary to carry out the experiments in alcoholic solution because of the insolubility of the substances in water.

Pyrantin (m. p. 155°)	Ac=0·0949
Methylpyrantin (m. p. 105—106°)	Ac=0·1831
as-Dimethylpyrantin (m. p. 70—71°)	Ac=0·0872
cis-s-Dimethylpyrantin (m. p. 114—115°) ..	Ac=0·1393
Trimethylpyrantin (m. p. 87—88°)	Ac=0·0446
*iso*Propylpyrantin (m. p. 98—99)	Ac=0·1432

The stability constant was determined for phenylsuccinimide in both aqueous and alcoholic solution, in order to compare the results obtained with those of Miolati for the tolyl- and xylyl-succinimides in aqueous solution.

Phenylsuccinimide was found to be 40·03 times more stable in alcoholic than in aqueous solution, and a correction had also to be made for the value of the ethoxyl group which decreased the stability in alcoholic solution 1·704 times.

The results can then be calculated and tabulated, for the methyl substituted phenylsuccinimides.



	Ac found. Pyrantin in alcoholic solution.	Ac calculated. Phenyl-succinimide in alcoholic solution divided by 1·704.	Ac calculated. Phenyl-succinimide in aqueous solution (G. and S.) multiplied by 40·03; or found (Miolati).
Pyrantin	0·0949	0·0557	2·23
Methylpyrantin ..	0·1831	0·1075	4·30
Isopropylpyrantin ..	0·1432	0·0840	3·36
cis-Dimethylpyrantin	0·1393	0·0818	3·27
Phenylsuccinimide ..	Mean of both Miolati and authors' experiments.		2·23
as-Dimethylpyrantin	0·0872	0·0512	2·05
3:5-Xylylsuccinimide	—	—	1·145
p-Tolylsuccinimide..	—	—	1·12
m- ,, ..	—	—	1·10
Trimethylpyrantin ..	0·0446	0·0262	1·05
2:5-Xylylsuccinimide	—	—	0·88
o-Tolylsuccinimide..	—	—	0·856
2:3-Xylylsuccinimide	—	—	0·815
2:6- ,,	—	—	0·16

A glance at the above table easily shows in how great a degree the stability of the succinimide ring can be decreased by the introduction of methyl groups into the fatty ring, whereas Miolati's experiments prove that the introduction of methyl groups into the aromatic nucleus increase the stability.

Substances having the constitution formulated above but containing methyl groups in both rings do not appear to have been prepared, although the list given is long enough to anticipate the result which might be expected in such cases.

The reason the authors chose the pyrantins and calculated the results was that they might obtain some information about the antipyretic action of the methyl group, but unfortunately the substances obtained proved so insoluble in water that no definite result has been obtained.

174. "*Experiments on the Production of Optically Active Compounds from Inactive Substances.*" By F. Stanley Kipping, Ph.D., D.Sc., F.R.S.

The note by Cohen and Whiteley under the above title (*Proc.*, p. 212), deals with experiments which are very similar to some in which the author, assisted by Mr. Hunter, has been recently engaged, the results of which it thus becomes desirable to place on record.

Guided by practically the same considerations, and working with the same object as Cohen and Whiteley, attempts have been made to prepare directly unequal quantities of two enantiomorphously related substances by synthesising an asymmetric carbon group in presence of, or in combination with, some optically active compound, in the hope that the latter would have some directive action on the atoms or groups entering into combination.

Among those experiments in which an optically active substance was used merely as a medium in which the synthesis took place, mention may be made of the preparation of benzoin by the action of potassium cyanide on benzaldehyde in a concentrated alcoholic solution of camphor; mandelic nitrile was also prepared from benzaldehyde and hydrogen cyanide in an alcoholic solution of camphor, and then hydrolysed with hydrochloric acid; pyruvic acid and methyl ethyl ketone were also separately reduced in concentrated glucose solution. The results were negative in all these cases.

Among the experiments in which the optically active substance was combined with the inactive nucleus the following may be noted:—The reduction of quinine pyruvate and of quinine lævulinate with sodium amalgam or aluminium amalgam; the reduction of *bornyl pyruvate* (b. p. 149—150°, 15 m.m.); the reduction of the *oxime* (m. p. about 90°) of bornyl pyruvate, and the reduction of bornyl lævulinate (b. p. 170—171°, 20—25 m.m.). After eliminating the original optically active base or alcohol, the product, namely, lactic acid, α-amidopropionic acid, or γ-hydroxyvaleric acid (as lactone), as the case might be, was found to be inactive.

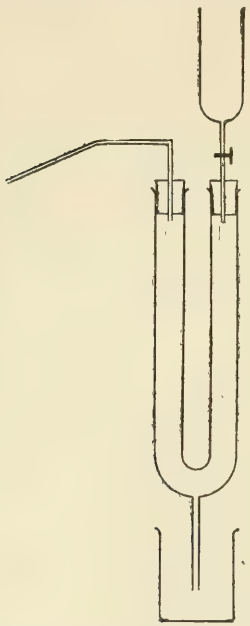
Owing to its low specific rotation and the difficulty of isolating it, the experiments in which lactic acid was obtained are by no means satisfactory, and mandelic acid, which has a high specific rotation, was therefore prepared by the reduction of *bornyl benoylformate*; this ethereal salt separates from light petroleum in crystals melting at about 78°, and is reduced to the corresponding hydroxy-salt by sodium amalgam in presence of a little acetic acid; after hydrolysis with potash, it gave inactive mandelic acid.

The failure of these experiments may be caused by racemisation taking place during hydrolysis of the original product, and this possibility is being investigated; even the apparently strong evidence obtained by combining these results with those of Cohen and Whiteley can hardly be considered to settle the question as to the possibility of directly synthesising *unequal* quantities of enantiomorphously related forms, in view of the actual results obtained in the case of the sugars, and the theoretical conclusions by which they may be supported.

175. "*A Lecture Table Experiment for the Preparation of Nitric Oxide.*" By Alfred Senier.

When nitric oxide is prepared by the interaction of copper and diluted nitric acid in a flask in the ordinary way, a difficulty arises owing to the accumulation of water. This gives rise to the formation of a large propor-

tion of nitrous oxide. By employing concentrated nitric acid and an excess of copper in the apparatus shown this may be obviated. The figure explains itself. In the apparatus employed the U-tube has a diameter of 3 c.m., and together with the small tube beneath measures 36 c.m. in height. The larger tube is loosely packed with copper turnings, water is put into the beaker below, and



nitric acid (68 per cent), is dropped from the stoppered funnel. Each drop of acid acts on the copper, liberating nitric oxide, while a solution of cupric nitrate and dilute nitric acid passes into the beaker. The gas after ascending the second arm of the U-tube is quite colourless, and contains only traces of nitrous oxide as shown by absorption with ferrous sulphate.

(To be continued).

NOTICES OF BOOKS.

Evolution of the Thermometer, 1592—1743. By Henry Carrington Bolton. Easton, Pa.: The Chemical Publishing Company. Edinburgh: W. F. Clay. 12mo. Illustrated. 1900.

In this attractive little book the author has undertaken to sketch in an impartial way the history of the evolution of the thermometer from its first beginnings in Italy, through its crude early forms down to the three standards now commonly used in all enlightened countries. The author shows how the Italian physician Sanatorius wrote in 1613 to his friend Galileo of his employment of the instrument "which you invented." This establishes the fact that Galileo was the actual inventor of the open air-thermoscope sometime prior to 1595. The claim for Drebbel is examined and proved to be a myth.

Nearly fifty years after Galileo the thermometer was rendered independent of the pressure of the air by Ferdinand II., Grand Duke of Tuscany, who closed the glass tube partially filled with coloured alcohol, and seventy years more elapsed before reliable and comparable thermometers were introduced.

The author traces the long series of efforts made by Robert Hooke, Hon. Robert Boyle, the famous Academy of Experiments in Florence, Newton, and Amontons, to devise convenient and reliable fixed points for a standard scale, efforts that finally were crowned with success by Fahrenheit. He gives credit to Jean Rey (the author of the treatise: "Why do Lead and Tin increase in Weight when Calcined?"), for first constructing a thermoscope containing water as the dilating liquid; to Fabri for dividing the interval between the temperature of snow and of midsummer heat; and to Renaldini for first proposing the freezing- and boiling-points of water as fixed points in the scale. The improvements made in thermometers by Réaumur and by Celsius are briefly described.

The author has evidently taken pains to consult the best and earliest authorities on the early history of the thermometer, a list of which occupies the latter pages of the volume; the Chronological Epitome and the table of thirty-five thermometer scales will be found useful.

The book is clearly printed on heavy paper, and tastefully bound in two shades of blue. The illustrations are appropriate. There is an index.

CORRESPONDENCE.

DETECTION OF ARSENIC.

To the Editor of the Chemical News.

Sir,—Concerning the use of aluminium and sodium hydrate in the Berzelius-Marsh test for arsenic, it may be well to point out that minute quantities of arsenic are not evolved as AsH_3 from an alkaline solution. While with perfectly pure zinc and boiled hydrochloric acid as little as 0·005 m.grm. of arsenious acid gives a distinct mirror, I have not been able to get any indication of a mirror with Al and NaOH and 0·01, 0·05, 0·1, and 0·2 m.grms. of arsenious acid in about 25 c.c. of solution. I have not ascertained the minimum amount of arsenic which will show under these circumstances. It is, however, possible that, as various kinds of pure zinc vary widely as to their sensitiveness to the test, so different samples of aluminium may show a similar behaviour.

I have found it quite necessary to test every batch of new material, after absence of arsenic was proved, for sensitiveness, and to prepare from every batch comparison-mirrors.—I am, &c.,

Otto Hehner.

The Laboratory,
11, Billiter Square, London, E.C.,
January 12, 1901.

Carbide of Calcium as a Reducing Agent in Analyses by the Dry Way.—M. Tarugi.—At about 1400° carbide of calcium reduces the oxide and the salts of copper, forming a calcic alloy which loses its calcium by the action of hydrochloric acid. Lead also forms an alloy. The salts of Au, Ag, Pt, Sn, Bi, Sb, Cd, Zn, Ni, and Co, whatever they may be, give an alloy of the metal with calcium, at a red heat: the alloy is easily decomposed by water. The salts of Hg and As give the free element Hg or As. It would be of advantage, in fire analysis, to heat the substance with 5 parts of carbide in a test-tube, instead of using the old method of reduction in the flame, or by means of cyanide of potassium.—*Gazz. Chim. Ital.*, xxix. p. 509.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, del'Académie des Sciences. Vol. cxxxi., No. 26, December 24, 1900.

The Origin of Chemical Combination. Union of Silver with Oxygen.—M. Berthelot.—The author performed various experiments, the results of which throw a new light on the formation and the decomposition of silver oxide. A known weight of pure silver was introduced into a hard glass tube, the end of which was drawn off. A gas, such as oxygen, air, hydrogen, nitrogen, carbon dioxide, carbon monoxide, or water vapour, was then introduced into the tube and the end sealed. The tube was heated to a definite temperature for some hours, after which a complete analysis of the gas was made, with an examination of the metallic substance.

Silver and Carbonic Oxide.—M. Berthelot.—Experiments made with carbonic oxide in presence of silver, show that the deposition of carbon appears at a lower temperature than if the gas were alone. The author's explanation of this phenomenon becomes very simple, since the discovery of the property of carbonic oxide of combining with nickel or iron to form volatile compounds. In contact with silver, a precipitation of carbon takes place at about 300°, and the simultaneous disintegration of the silver seems to show that this double phenomenon is the consequence of the beginning of the formation of a compound analogous to iron carbonyl.

Hydrogen and Silver.—M. Berthelot.—When hydrogen is kept in presence of silver at 500—550° in a sealed tube for five hours, indications of disintegration and traces of powder show themselves; much less marked, however, than when oxygen or carbonic oxide are used, but contrasting strongly with the inalterability of the metal kept at the same temperature in presence of pure nitrogen, carbonic acid, or water-vapour. It is probable that the change stated above is due to the slight formation of metallic hydride.

Rarefied Gases.—Albert Colson.— Red and yellow oxides of mercury were examined by the author in vacuum tubes exhausted from air. He finds that the red oxide of mercury is less alterable than the yellow oxide, but that both these are reduced by the glass. He carefully ascertained whether this influence was due only to the chemical composition of the glass, or if hydrogen—of which Armand Gautier has shown a decided quantity in atmospheric air—is capable of passing through the glass, or if the intimate contact of such a substance, glass or powder, sur-excites the activity of the hydrogen, as HCl or H_2O sur-excites that of fluorine in M. Moissan's experiments. The author's researches confirm the fact that, apart from all electric or luminous excitement, the glass emits the reducing gases, which are renewed in proportion to their absorption, as if they possessed a fixed tension, and of which the reducing power exceeds that of free hydrogen.

Influence of Pressure in Phenomena of Chemical Equilibrium.—O. Boudouard.—The author has shown in a previous paper that the numerical results obtained during the investigation of the reversible reaction $2CO \rightleftarrows CO_2+C$ verify the formula giving the general law applied to the equilibrium of gaseous systems at all temperatures, but in this verification the pressure did not alter during the experiments. The author now shows that whilst operating at pressures differing from atmospheric pressure, the results obtained still verify the formula.

Copper Selenides.—M. Fonzes-Diacon.—The author prepares cupric selenide, CuSe, by new methods. He also obtains cuprous selenide, by the wet method, in the form of a green precipitate; this same compound, in a perfectly crystalline form, can be prepared by the reduction of cupric selenide by means of hydrogen, by the reduction of copper selenate by carbon, and by the action of seleniuretted hydrogen on the chlorides of copper at a high temperature.

Some Chlorobromides of Thallium.—V. Thomas.—In a previous paper the author drew attention to the action which bromine has on thallous chloride, and announced the existence of chlorobromides belonging to one of the following types of compounds:—Tl_2X_3, TlX_2, and TlX_3. The present paper contains an account of researches on chlorobromides of the type Tl_2X_3, obtained directly by the action of bromine on the chloride TlCl in presence of water.

Action of Reducing Agents on the two Isomeric Nitrodimethylacrylic Ethers.—L. Bouveault and A. Wahl.—In two preceding papers the authors have shown that the direct nitration of ethyl dimethylacrylate results in a nitrogen derivative of constitution $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C=C(NO_2)\!-\!COOC_2H_5$. This latter substance, when treated with alcoholic potash, gives the potassium derivative of an isomeric nitrogen derivative, $\begin{matrix}CH_2\\CH_3\end{matrix}\!\!>\!C\!-\!CH(NO_2)\!-\!COOC_2H_5$. The authors have since tried the action of various reducing agents on these two substances.

Uranium Nitrate.— Œchsner de Coninck.—A very pure salt, possessing the normal composition, was employed for the author's experiments. He first determined the density of some solutions of this material in water and in dilute ethyl alcohol; he then ascertained in what media this uranium nitrate was soluble, and measured the solubility in water for temperatures in the neighbourhood of 15° and the heat of solution in the same substance; the latter number, determined at temperatures 17·5° and 18·2°, gives as a mean result −3·8 cal. The author is continuing these researches.

Reaction of *p*-Diazobenzene Sulphonate of Sodium on Iron Cystinate existing in Contaminated Waters.—H. Causse.—Referring to the work of M. Molinié on this subject, the author states that he cannot accept any of Molinié's conclusions. The above reaction is characteristic rather of a group than of a substance. When the waters contain ferrous combinations containing the group CSH or COS, they give the positive reaction not destroyed by sulphuric acid. The polyatomic phenols, resorcine, pyrocatechine, and ordinary phenol present the same peculiarities with characteristic colours. The two groups CSH and COS, being most certainly the result of putrid fermentations, can show the relation which ought to exist between the degree of contamination of a water and its action of the reagent, as well as the services which this reagent renders in analysis.

Some Derivatives of Methylnonylketone. — H. Carette.—Methylnonylketone, when pure, is colourless and non-fluorescent, contrary to previous statements. It boils at 230·6° under a pressure of 766 m.m., at 122° under a pressure of 24 m.m., and at 112° under that of 17 m.m. The author prepares the oxime of this ketone, and also studies the products of condensation of methylnonylketone with benzoic aldehyde. The first process of condensation consists in the elimination of a molecule of water, $C_{11}H_{22}O+C_7H_6O=H_2O+C_{18}H_{26}O$. The second process of condensation with benzylal results in a new product fusible at 116° and having the formula $(C_{18}H_{26}O)_2$.

Chemical Transformations which take place during the Evolution of a Bud.—G. André.

Tannase.—A. Fernbach.

Tannase. Splitting-up of Gallotannic Acid by Diastase.—Henri Pottevin.

MISCELLANEOUS.

New Method for the Separation of the Earths of Gadolinite, and the Preparation of Pure Yttria.—W. Muthmann and R. Böhm.—This process consists of fractional precipitation in the form of chromate. To carry this out the mixture of the rare earths in the form of oxides is triturated with more than double its weight of CrO_3, and diluted with a large quantity of water. A lively reaction takes place, the whole going into solution in the form of bichromate. The solution is placed in a large retort and brought to boiling point, while at the same time steam is passed continually through the mass, and a solution of CrO_4K_2 is added drop by drop, the amount added being an aliquot part of the quantity necessary for complete precipitation. The authors have in this manner treated a sample of commercial *pure Yttria*, operating in six portions. The true yttria was collected in the two last fractions; in less than a fortnight they obtained 15 per cent. of the original mixture in a state of perfect purity.—*Berichte*, vol. xxxiii, p. 42.

Citrate of Lime and its Analysis.—A. Soldaini and E. Berté.—Citrate of lime comes principally from Sicily, whence it is exported in large quantities, principally to England, for the manufacture of citric acid. 10,000 lemons—that is, about 1000 kilogrms. of fruit—give 3·7 kilogrms. of essence and 400 litres of juice, from which 30 to 31 kilogrms. of citrate, containing 64 to 66 per cent of citric acid, are precipitated by means of lime. The residual pulp, weighing about 500 kilogrms., serves as food for cattle. The analysis is generally made by the precipitation of a pure citrate of calcium or lead. In the latter case the precipitate is decomposed by H_2S, and the citric acid set free can be titrated. These two methods give differences of 2 per cent on a commercial citrate; it would, therefore, be of great advantage to adopt one well-proved method, which could be relied upon for commercial analyses. The lime process, which is the better of the two, should be carried out as follows:—One grm. of the moderately powdered sample is rubbed up with 10 c.c. of warm water, then treated with 20 drops of hydrochloric acid, neutralised in the cold with N/2NaOH in the presence of phthalein until the rose-colour remains, and then treated with 3 c.c. of acetic acid. The solution is filtered, and, with the washings, evaporated to dryness on the water-bath in a porcelain crucible; it is then taken up with 20 c.c. of boiling water, well rubbed up, filtered, and carefully washed with 55 c.c. of water, dried and calcined for ten minutes, and the CaO weighed. A grave source of error is to attempt to dissolve the citrate in acetic acid. The pure salt is not entirely soluble; this gives rise to too low results. Pure citrate of lime is hygroscopic.—*Gazz. Chim. Ital.*, xxix., p. 489.

MEETINGS FOR THE WEEK.

Monday, 21st.—Society of Arts, 8. (Cantor Lectures). "Elementary Art Education," by J. Liberty Tadd.

Tuesday, 22nd.—Royal Institution, 3. "Practical Mechanics" (Experimentally treated), by Prof. J. A. Ewing, M.A., F.R.S., M.Inst.C.E.

—— Society of Arts, 4.30. "The Commonwealth of Australia," by the Hon. Sir John Alexander Cockburn, K.C.M.G.

Wednesday, 23rd.—Society of Arts, 8. "The proposed High-speed Electrical 'Monorail' between Liverpool and Manchester," by F. B. Behr.

Thursday, 24th.—Royal Institution, 3. "The Origin of Vertebrate Animals," by Arthur Willey, M.A., D.Sc.

Friday, 25th.—Royal Institution, 9. "Some Aspects of Seventeenth Century Pietism," by Adolphus William Ward, Litt.D., LL.D.

—— Physical, 5. "The New Physical Laboratories of the Royal College of Science," by Prof. A. W. Rücker, Sec.R.S. "Note on the Absolute Method Method for Determining the Hygrometric State of the Atmosphere," by E. B. H. Wade, M.A. Exhibition of an Experiment on the Migration of the Ions, by S. W. J. Smith.

Saturday, 26th.—Royal Institution, 3. "The Government and People of China," by Prof. R. K. Douglas.

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THE CHEMICAL NEWS.

VOL. LXXXIII., No. 2148.

THE PHOSPHATE METHOD FOR THE ESTIMATION OF MANGANESE AND COBALT.

By H. D. DAKIN.

IN a former paper on "The Estimation of Zinc as Phosphate" (*Zeitschrift fur Analytische Chemie*, vol. xxxix., p. 273; also CHEMICAL NEWS, vol. lxxxii., p. 101) a modified process was described, which was capable of effecting quantitative conversion of tribasic zinc phosphate into zinc ammonium phosphate, without the aid of large quantities of ammonium salts, the presence of the latter having previously been stated to be essential. The object of the following note is to show that a similar method to that adopted in the case of zinc is applicable to the estimation of manganese and of cobalt.

The phosphate process has frequently been stated to be the most accurate of the different methods employed to bring manganese compounds into a readily weighable form. Recently the method has been re-examined by Gooch and Austin (*Amer. Journ. Sci.*, vi., p. 233), who, from the results of a large number of analyses, consider that the method as ordinarily described is subject to a grave source of error, in that, unless very large quantities of ammonium salts are present, the precipitate first thrown down when an alkaline phosphate is added to a solution of a manganese salt, is incompletely converted into manganese ammonium phosphate, and hence low results are obtained. This being so, it seemed of interest to see if the process adopted in the case of zinc was suitable for the estimation of manganese, especially since difficulties are said to attend the precipitation of zinc ammonium phosphate precisely similar to those encountered in the case of manganese.

For the experiments that follow pure sulphate of manganese was used. The salt was twice re-crystallised, and the small crystals dried on porous tiles. The proportion of manganese in it was determined by observing the weight of anhydrous $MnSO_4$ yielded by a known weight of the salt on gentle ignition. The ignition was performed in a similar way to that recommended by Gooch and Austin (*Amer. Journ. Sci.*, v., p. 209). The weighed salt, with the addition of a drop or two of strong sulphuric acid, was contained in a platinum crucible, the latter being jacketed with another larger crucible, containing a support at the bottom, so that the crucible containing the salt would not come into contact with the more strongly heated part of the arrangement. The method was found to give excellent results with manganese compounds of known composition. Duplicate determinations differed by less than 0·01 per cent of manganese.

The estimations were carried out as follows:—A known weight of the manganese sulphate was dissolved in 100 to 150 c.c. of hot distilled water, and, to the solution contained in a platinum basin, excess of hydrogen di-ammonium phosphate added, equal to from ten to twenty times the weight of metal present. The liquid was then heated on a water-bath, when the amorphous tri-basic manganous phosphate first thrown down is rapidly converted into beautifully crystalline manganese ammonium phosphate. No ammonium chloride or other salt was added to the solution. At the end of ten to fifteen minutes the liquid was allowed to cool, and after half an hour or more filtered, using the Gooch crucible with as small an asbestos felt as is possible to combine with efficient filtration. The precipitate was then washed with a hot 1 per cent ammonium phosphate solution. When washed free from sulphates, the small amount of phosphate solution adhering to the precipitate was removed by a few washings with dilute re-distilled alcohol. The crucible and contents were then dried, ignited, and weighed. The ignition was performed with free access of air, so as to allow of the ready escape of ammonia and water-vapour, since there is a possibility of the ammonia being partially decomposed into its elements and the liberated hydrogen reducing the pyrophosphate, and so leading to low results.

Table I. illustrates the accuracy of the process.

It will be seen that the numbers obtained agree fairly closely with those required by theory. The filtrates were in all cases tested for manganese, in some with bromine and ammonia, in the remainder with ammonium sulphide. In one case only was a minute trace found, this doubtless

TABLE I.

No.	$MnSO_4$=Mn taken.	$Mn_2P_2O_7$ obtained.	=Mn found.	Error.	$(NH_4)_2HPO_4$ present. Grms.	Mn in filtrate.
1.	0·2966	0·7656	0·2965	−0·0001	2·5	None
2.	0·2040	0·5277	0·2043	+0·0003	2·5	,,
3.	0·1911	0·4940	0·1913	+0·0002	2·0	,,
4.	0·1713	0·4426	0·1714	+0·0001	1·6	,,
5.	0·1668	0·4331	0·1677	+0·0009	3·4	,,
6.	0·1550	0·4003	0·1550	—	1·6	,,
7.	0·1249	0·3220	0·1247	−0·0002	1·3	Trace
8.	0·1226	0·3168	0·1227	+0·0001	1·2	None
9.	0·0906	0·2351	0·0910	+0·0004	0·8	,,
10.	0·0834	0·2142	0·0830	−0·0004	0·8	,,
11.	0·0750	0·1944	0·0752	+0·0002	1·4	,,

TABLE II.

Time of drying. Hours.	Expt. 1. Grm.	Expt. 2. Grm.	Expt. 3. Grm.	Expt. 4. Grm.
1	0·6918	0·4142	0·5806	0·3448
2	0·6916	0·4142	0·5806	0·3448
5	0·6915	0·4141	0·5806	0·3448
10	0·6916	0·4141	—	0·3448

TABLE III.

No.	$MnSO_4$ =Mn taken. Grm.	$MnNH_4PO_4H_2O$ obtained.	=Mn found.	Error.	$(NH_4)_2HPO_4$ present. Grms.	Mn in filtrate.
1.	0·2966	1·0039	0·2966	—	2·5	None
2.	0·2040	0·6916	0·2043	+0·0003	2·5	,,
3.	0·1911	0·6482	0·1915	+0·0004	2·0	,,
4.	0·1713	0·5806	0·1715	+0·0002	1·6	,,
5.	0·1550	0·5241	0·1549	−0·0001	1·6	,,
6.	0·1249	0·4205	0·1243	−0·0006	1·3	Trace
7.	0·1226	0·4154	0·1228	+0·0002	1·2	None
8.	0·0834	0·2815	0·0832	−0·0002	0·8	,,
9.	0·0750	0·2554	0·0754	+0·0004	1·4	,,

TABLE IV.

No.	Cobalt taken.	$CoNH_4PO_4H_2O$ obtained.	=Cobalt found.	Error.
1.	0·2203	0·7104	0·2205	+0·0002
2.	0·1314	0·4220	0·1310	−0·0004
3.	0·1255	0·4040	0·1254	−0·0001
4.	0·0831	0·2684	0·0833	+0·0002
5.	0·0587	0·1892	0·0587	—

TABLE V.

No.	Cobalt taken.	$Co_2P_2O_7$ obtained.	=Co found.	Error.
1.	0·2203	0·5454	0·2204	+0·0001
2.	0·1314	0·3242	0·1310	−0·0004
3.	0·1255	0·3109	0·1256	+0·0001
4.	0·0831	0·2058	0·0831	—
5.	0·0587	0·1448	0·0585	−0·0002

being due to imperfect filtration or some other mechanical cause. No difference could be detected in the results whether the time allowed for precipitation extended over half an hour or twenty-four hours.

The main points on which the accuracy of the process depend are:—

(1). The use of a sufficiently large excess of ammonium phosphate.

(2). Thorough washing with hot 1 per cent phosphate solution.

In some analyses, in which these conditions were not adhered to, the results were some 3 m.grms. too low. The best proportion of ammonium phosphate to employ is about fifteen to twenty times the weight of manganese present, although good results may be obtained with less than this quantity, as may be seen from the test analyses. In estimating zinc as phosphate, the precipitate may be weighed either as $Zn(NH_4)PO_4$, dried at 100° C., or as ignited $Zn_2P_2O_7$. As far as I am aware, the corresponding manganese precipitate has always been converted into the pyrophosphate; it therefore seemed of interest to see whether it also might be weighed as the double ammonium salt. Experiments showed that good results were to be obtained in this way. The manganese precipitate differs from the zinc, however, in that it contains an additional molecule of water, which, even at very prolonged heating, at a temperature of 100° to 105° C., does not affect. The precipitate rapidly attains a perfectly constant weight, as is shown in Table II.

The numbers given represent the weights of the different precipitates dried for the length of time indicated.

The results obtained when the precipitate was weighed as the double ammonium phosphate are tabulated in Table III.

The results will be seen to be tolerably accurate, the error usually being less than half a m.grm.

The numbers for the amount of manganese, as calculated both from the weight of $MnNH_4PO_4.H_2O$ and of the $Mn_2P_2O_7$, agree very well with each other, so that the one method may safely be used to supplement the other.

Moreover, if the figures obtained in the two ways agree, fairly conclusive proof is afforded of the fact that the precipitates were of correct composition, and hence that the tri-basic manganese phosphate was completely converted into the double salt in the first instance. Ammonia determinations made on precipitates obtained in the same way as in an actual analysis yielded results differing by only two or three hundredths of a per cent from the theoretical amount. In the practical application of the process, the liquid containing the manganese must previous to precipitation be freed from any large excess of acid; but there is no necessity for the solution to be absolutely neutral, provided sufficient phosphate is used. The subsequent operations are identical with those previously described, and are, I think, simpler than those usually recommended.

The conclusion is drawn that, when the analysis is conducted as described, even in the absence of large amounts of ammonium salts, the precipitate obtained corresponds strictly to formula, and that good results may be obtained whether the manganese is weighed either as the pyrophosphate or as the double ammonium salt.

The accuracy of so many processes for the determination of metals as phosphates having been called in question during recent years, it seemed of interest to see if the modified process, as used for zinc and manganese, was also of use in estimating other metals. The determination of cobalt as phosphate has long been a well-recognised method specially useful in the presence of nickel. The cobalt used in the subsequent analyses was purified as follows:—A solution of the nitrate was acidified with acetic acid and filtered, and to this a clear solution of potassium nitrite in dilute acetic acid added, and then, before all the cobalt was precipitated, the double nitrate of potassium and cobalt was filtered off and well washed. The yellow precipitate was then decomposed by means of pure sulphuric acid, all nitrous fumes being expelled; the solution was then fractionally precipitated as carbonate. The precipitate was filtered off, washed, and dried, and the amount of cobalt in it determined by conversion into sulphate and also by analysis.

The analyses were conducted in the same way as in the case of manganese. A known weight of the cobalt carbonate was dissolved in dilute sulphuric, and the solution nearly neutralised with ammonia; di-ammonium hydrogen phosphate, equal to ten times the weight of cobalt present, was then added. At first an amorphous violet precipitate was thrown down, and this quickly changes into deep blue, and finally into the beautifully crystallised crimson cobalt ammonium phosphate. The liquid should be kept hot for ten minutes or so, then cooled and filtered, the precipitate being washed with hot 1 per cent ammonium phosphate solution, and then with dilute alcohol. In the same way as in the case of manganese, it was found that the precipitate could be weighed quite well, as the double salt dried at 100° to 105°, in addition to the pyrophosphate. Tables IV. and V. illustrate the accuracy of the method.

The filtrates were tested and found free from cobalt. The results will be seen to be equally accurate whether the precipitate be weighed as cobalt ammonium phosphate, $(CoNH_4PO_4.H_2O)$, or as cobalt pyrophosphate, $(Co_2P_2O_7)$. Hence it may be concluded that no difficulty is introduced into the estimation of cobalt as described, by any uncertainty in the composition of the precipitates obtained.—*Zeitsch. f. Anvlyt. Chem.*, xxxix., p. 784.

A BIBLIOGRAPHY OF STEEL WORKS ANALYSIS.

Part VII.

By HARRY BREARLEY.

(Continued from vol. lxxxii., p. 307).

CHROMIUM.

THE general arrangement is—

I. Separation from other Elements.

II. Gravimetric Estimation.
- *a.* In which Cr is the Base of the Weighed Salt.
- *b.* ,, ,, Acid ,, ,,

III. Volumetric Estimation.
- *a.* Titrating with Ferrous Salt.
- *b.* Iodometrically.
- *c.* Miscellaneous Processes.

IV. Means of Converting to CrO_3.
- *a.* Dry Ways.
- *b.* Wet Ways.

V. Detection of Chromium.

VI. Miscellaneous Notes.

I. Separation from other Elements.

Iron.—

946. Gibbs (*C. N.*, xi., 101).—Oxidise to CrO_3 and precipitate Fe with acetate or AmHO. Similar process for Al.

947. Baubigny (*C. N.*, l., 18).—Ignited chromite oxidised with HNO_3+KClO_3, and Fe and Al precipitated by a slight excess of bicarbonate. The CrO_3 reduced with H_2S and precipitated as hydrate.

948. Brearley (*C. N.*, lxxvii., 49). — Separation from CrO_3 with acetates or alkalis the more complete the greater excess there is used. Deficiency due to basic ferric chromates. NaHO the best precipitant.

949. Knorre (*C. N.*, lix., 232).—Iron precipitated from HCl solutions with nitroso-β-naphthol. The Cr in the filtrate cannot be completely precipitated with AmHO.

950. Hess and Campbell (*C. N.*, lxxxi., 159).—Cr is precipitated quantitatively from solutions containing Fe, Ca, Mg, Mn, Co, and Ni by phenylhydrazine.

951. Boussingault (*J. I. S. I.*, 1886, 828).—Fe and Cr cannot be separated by heating in HCl gas, because Cr_2O_3 is thus volatilised (see 961). Havens and Way (*J. S. C. I.*, 1899, 1157) say the separation can be made at 200—300° in a stream of HCl containing Cl.

952. Venator and Etienne (*J. C. S.*, liii., 532).—Decompose the mineral with NaHO, evaporate solution of the fusion, and leach Na_2CrO_4 from the dried mass.

953. Bamber (*J. I. S. I.*, 1894, i., 319).—Add Na_2CO_3 short of alkalinity to the HNO_3 solution of the iron, evaporate, ignite, and dissolve out Na_2CrO_4 with water.

954. Jannasch and Cloedt (*J. C. S.*, lxx., ii., 222).—Mix with H_2O_2+AmHO, and heat under pressure. The filtered CrO_3 is reduced and precipitated with hydroxylamine chloride and ammonia.

Aluminium.—

955. Carnot (*C. N.*, xliv., 85).—The Al is precipitated from CrO_3 solution with soda phosphate and acetate.

956. Brearley (*C. N.*, lxxvii., 179).—Similar paper to 948. Na_2CO_3 the best alkaline precipitant; Na_3PO_4 available.

957. Hunt, Clapp, and Handy (*C. N.*, lxv., 223).—Cr-Al alloys are boiled with KHO; residue fused with $KHSO_4$, converted to CrO_3, but finally precipitated with AmHO.

Chromic Acid.—

958. Storer and Elliot (*C. N.*, vi., 121).—Precipitate Cr_2O_3 from dilute acid solution with AmHO.

959. Brearley (*C. N.*, lxxvii., 217).—Preceding process inaccurate. Separate with NaHO or Na_3PO_4.

Uranium.—

960. Gibbs (*C. N.*, xxviii., 63).—Oxidise to CrO_3, and precipitate Ur with NaHO, or the CrO_3 may be precipitated with $HgNO_3$ if no other precipitable non-volatile body is present.

961. Ditte (*C. N.*, xxxvi., 100).—The oxides of Fe, Cr, and Ur are heated in H and then in HCl to volatilise the Fe (see 951). Dissolve Ur from the residue with HNO_3.

962. Formanek (*J. C. S.*, liv., 531).—To precipitate the CrO_3 with $HgNO_3$ (960) is inaccurate. Ditte's process is also unsatisfactory.

Vanadium.—

963. Classen (*J. I. S. I.*, 1887, i., 473).—Precipitate together as lead salts, eliminate Pb from HCl solution with H_2S, fuse evaporated filtrate with NaHO and S, and extract V with water.

964. Von Klecki (*C. N.*, lxix., 54).—Precipitate V with uranic nitrate from an acetic solution.

965. *Copper.*—Prud'homme (*C. N.*, xxv., 215).—From a mixture of the oxides of Cu and Cr the Cu is dissolved by NaHO, but both oxides are dissolved by AmHO.

966. *Phosphorus.*—Granger (*C. N.*, lxxv., 95).—Fuse with KHO, dissolve, acidify with HNO_3, and precipitate with molybdate.

967. *Mercury.*—Jannasch (*J. C. S.*, lxxvi., ii., 6c).—Precipitate the Hg with hydroxylamine in the presence of oxalic acid.

II. Gravimetric Estimation of Chromium.

II.*a. Where Cr is the Base of the Weighed Compound.*—

968. Oudesluys (*C. N.*, v., 254).—Add Na_2CO_3+KNO_3 to the $KHSO_4$ fusion, precipitate Al_2O_3 with Am_2CO_3, reduce, precipitate with AmHO, and ignite to Cr_2O_3.

969. Genth (*C. N.*, vi., 31).—As above; but omit the KNO_3, and precipitate Al_2O_3, &c., by boiling with excess $AmNO_3$.

970. Cloubt (*C. N.*, xxiv., 304).—Fuse ore for six hours with Na_2CO_3, reduce CrO_3 with alcohol, and precipitate with AmHO.

971. Tamm (*C. N.*, xxiv., 305).—In general like 968; but the CrO_3 is reduced with HCl, and the nitrous oxide evolved (see 1064).

972. Kern (*C. N.*, xxxv., 67).—Precipitate Fe and Cr together with Am_2S, ignite, fuse with K_2CO_3+KNO_3, and precipitate reduced filtrate with AmHO.

973. Waller and Vulte (*C. N.*, lxvi., 17).—Fuse with Dittmar's flux (1009), evaporate extract with $AmNO_3$, re-dissolve, reduce, and precipitate with AmHO. A resumé of the means of opening up chromites.

974. Ziegler (*C. N.*, lxvi., 295).—Fuse Fe-Cr with KHO+KNO_3 in silver crucible in smoky flame, pass CO_2, separate associated elements, and precipitate with AmHO. Instructions for estimating P, &c., in ferro-chromium.

975. Fresenius and Bayerlein (*C. N.*, lxxvii., 141).—Treat chromite with HCl; residue, with Na_2O_2. After various separations (Fe with Na_2O_2), reduce with H_2O_2, and precipitate with AmHO.

976. Namias (*J. I. S. I.*, 1890, ii., 853).—Fuse FeCr with $KHSO_4$, precipitate neutralised solution with MgO, ignite, re-fuse, and precipitate reduced solution with AmHO.

977. Morse and Day (*C. N.*, xliv., 43; and xlvii., 177).—Fuse powdered chromite with KHO in an iron crucible, separate Al_2O_3 with AmHO, reduce, and precipitate with $BaCO_3$.

978. Dohler (*J. S. C. I.*, 1899, 1157).—Precipitate with $BaCO_3$ from FeO solution, fuse, separate SiO_2, &c., and precipitate as usual (see 1010).

979. Reinhardt (*J. I. S. I.*, 1889, ii., 480).—Process based on the fact that Cr_2O_3 is precipitated by ZnO, while ferrous and manganous salts remain in solution.

980. Ziegler (*J. I. S. I.*, 1890, i., 372).—Decompose chromeisen with bisulphate, and proceed as 979, using hypophosphite to reduce the iron.

981. Kern (*C. N.*, xxxv., 107).—Fuse ore with $KHSO_4$, dissolve in HNO_3, add $(NH_4)HS$, dissolve Fe_2O_3 from the ignited precipitate, and weigh the Cr_2O_3 residue.

982. Jannasch and Mai (*J. C. S.*, lxiv., ii., 500).—In presence of hydroxylamine Cr_2O_3 is thrown down by ammonia as a violet-red precipitate, more easily washed than the green one.

983. Souchay (*C. N.*, xlvii., 248)—$Cr_2(HO)_6$ precipitated with AmHO in glass vessels is always too high.

984. Treadwell (*J. S. C. I.*, 1882, 339).—Cr may be precipitated in glass vessels by AmHO without error. The precipitate strongly retains fixed alkalis.

985. Bloxam (*C. N.*, liii., 194).—$Cr_2(HO)_6$ precipitated with AmHO carries down large amounts of MgO; also some SO_3.

986. Arnold (*C. N.*, xlii., 285).—Criticism of the volumetric process (1001). Decompose steel with acids, fuse dried residue with Na_2CO_3+KNO_3, reduce filtered CrO_3, and precipitate with AmHO.

987. Hogg (*J. S. C. I.*, 1891, 340).—Discusses process 1001. Proceeds as in 986. Oxidise ignited Cr_2O_3 with HNO_3+$KClO_3$ to separate SiO_2, &c., and finally precipitate with AmHO. Percentage approximated by comparing colour of samples dissolved in H_2SO_4. Paper washed with Br or Cl and AmHO does not reduce CrO_3 (see 1077).

988. Carnot (*C. N.*, xlv., 243).—Precipitate with soda acetate and phosphate from a slightly acid solution. The precipitate ignited and weighed.

989. Arnold and Hardy (*C. N.*, lvii., 153),—Cr_2O_3 obtained by (986 may contain P; it is better to precipitate the Cr as basic phosphate ($3Cr_2O_3.2P_2O_5$), which can be obtained of invariably the same composition.

II.*b*. *Where Cr is the Acid of the Weighed Compound.*—

990. Gibbs (*C. N.*, xi., 101).—Oxidise to CrO_3 with Cl or Br in acetate solution, and precipitate with Pb or Ba. Ca, Mg, Zn, Ni, Co, and Mn do not interfere. Precipitation with $HgNO_3$ should be made in the cold. Ore decomposed with potassium fluoride.

991. Gibbs (*C. N.*, xxviii., 63).—Berzelius's method (precipitation with $HgNO_3$) is best performed in hot solutions.

992. Baubigny (*J. S. C. I.*, 1884, 457).—Precipitation as Hg_2CrO_4 not advisable in presence of ammonia salts. Precipitates with Am_2S.

993. Schöffel (*C. N.*, xli., 31).—Treat with copper solution, fuse residue, and precipitate with $HgNO_3$; or remove SiO_2 and precipitate with Am_2S. High Cr irons not decomposed by Cu solutions; after fusion, a process like 1026 is used.

994. Boussingault(*J. I. S. I.*, 1886, 807).—Fuse with $KHSO_4$, precipitate Fe and Cr with AmHO, fuse with $Na_2CO_3+KNO_3$, and precipitate with $HgNO_3$.

995. Clark (*J. I. S. I.*, 1895, ii., 602).—Decompose ore with $KHSO_4$, oxidise with HNO_3+KClO_3, separate Fe and Al with AmHO, and precipitate as $PbCrO_4$.

(To be continued).

DETECTION OF LEAD IN POTABLE WATER.

By M. BELLOCQ.

Water containing the most minute traces of lead offers to the practised eye a faint though persistent opalescence which is destroyed by nitric acid; this fact gives rise to the opinion that the toxic metal may be in combination with some organic matter.

Of such a character are waters which have remained for a long time in new pipes, or in old pipes which have been disturbed by some repair or soldering; waters exposed, when in contact with lead, to the siliceous and carbonated dust of the air, are always contaminated with nitrated particles. For this reason the cleaning of lead pipes should be proscribed. Absolutely limpid water gives no trace of lead with my zinc reaction (*Journ. de Pharm. et de Chim.*, [6], xii., p. 103), and there is reason to believe that the hydrocarbonate is perfectly insoluble.

For the detection of lead I use a zincic reagent, in which the soda has been replaced by ammonia.

Add to 1 or 2 litres of suspected water an excess of ammoniacal zincic reagent (5 to 10 c.c.), and leave perfectly quiet for some hours. Decant as much of the supernatant water as possible (this should be absolutely limpid) and throw the rest on a filter, 15 or 18 c.m. diameter, for waters of average composition.

This filtration is very rapid, and the dried precipitate is very easily detached from the filter.

The precipitate is decomposed with warm acetic acid containing a little acetate of ammonia, and filtered in a small funnel, through a plug of absorbent cotton-wool, into a test-tube; the clear acid filtrate is touched with a glass rod wetted with a solution of chromate of potassium.

If the water contains lead a yellow cloudiness appears, and after the lapse of some time a precipitate of chromate of lead is formed.—*Journ. de Pharm. et de Chim.*, Series 6, vol. xiii., No. 2.

Royal Institution.—In consequence of the lamented death of the Queen, the Patron of the Royal Institution, the President has decided that all lectures shall be abandoned until further notice.

THE OXIDISING ACTION OF PERSULPHATE OF AMMONIA ON SOME DIRECT PRINCIPLES OF ANIMAL ORGANISMS.

By L. HUGOUNENQ.

When Berthelot discovered persulphuric acid he described the very remarkable oxidising properties of this compound. For some time past several alkaline persulphates have become articles of commerce. As a source of active oxygen they have a certain number of advantages. It is this that has decided me to study their action on substances of animal origin.

I. *Uric acid* is oxidised in the cold by persulphate of ammonia.

If we mix together 1 part of uric acid and 4 parts of persulphate with 12 parts of water at the ordinary temperature, or better still in an incubator at 36°, the uric acid completely disappears after seven or eight days. Allanturic acid, urea, and glycocol are formed.

In the presence of an excess of alkali the oxidising action of the persulphate is much more energetic. By causing 20 parts of this salt to act on 6 parts of uric acid in the presence of 150 parts of water and 30 parts of ammonia, the temperature rises, a lively effervescence takes place, and the liquid becomes yellow and limpid; all the uric acid has disappeared. From the filtered liquid we can separate:—

1. A quantity of guanine (from about 1 to 3 per cent of the uric acid attacked). The guanine has been recognised by all its reactions and by the estimation of the nitrogen; it already existed in the uric acid used, and from which it is very difficult to be removed.

2. A white, badly crystallised, not very stable, ammoniacal salt, which was recognised, on analysis, as allanturate of ammonia.

In the mother-liquors of this salt a small quantity of oxalate of ammonia is also found.

3. After the separation of the greater part of the sulphate of ammonia, alcohol extracts from the final residue a body which occurs in large, soluble, transparent prisms, which by means of its properties, as well as by its proportion of nitrogen, is identified as urea.

For 100 parts of uric acid oxidised we obtain about 42 parts of urea, and 27 or 28 parts of allanturate of ammonia.

To sum up, the persulphate oxidises uric acid in the same manner as peroxide of lead, ferrocyanide of potassium, permanganate, or ozone; allantoïne is formed, which in alkaline solution, and in the presence of an excess of an oxidising agent, is decomposed, giving urea and allanturic acid:—

$$\underset{\text{Allantoïne.}}{C_4H_6N_4O_3}+H_2O=\underset{\text{Urea.}}{CH_4N_2O}+\underset{\text{Allanturic acid.}}{C_3H_4N_2O_3}.$$

If we diminish the proportion of persulphate so as to obtain allantoïne itself, and not its products of decomposition, the reaction becomes difficult; the greater portion of the uric acid remains unattacked.

II. *Bilirubine* in alkaline solution is transformed instantaneously by persulphate of ammonia into biliverdine, and this is, as a matter of fact, the most simple and convenient method for the preparation of this latter pigment, as well as being at the same time an analytical test for bilirubine.

III. *Hematine*, in ammoniacal solution, is attacked even in the cold, but very quickly when heated. After boiling for two or three minutes the liquid, which was black at first, becomes colourless, and leaves flocculent particles of peroxide of iron.

It would be very simple to apply this reaction to the estimation of the iron in hematine, and doubtless also in hemoglobine and the ferruginous nucleins.

IV. Blood, diluted and treated with an excess of ammonia, is decomposed and decolourised in a few hours in the cold by persulphate of ammonia. A clear yellow liquid is obtained, and a slight ochreous deposit formed.

This result is obtained in a few minutes when heat is applied; the albumins then form a colourless coagulum, floating on an almost colourless yellowish liquid.

I propose continuing the examination of the products formed by the decomposition of hematine by persulphate of ammonia, and also to try and determine the manner of the action of this salt on the albumenoid matters which are also attacked.—*Journ. de Pharm. et de Chim.*, Series 6, vol. xiii., No. 2.

THE ALLOTROPIC FORMS OF SELENIUM.*

By A. P. SAUNDERS.

(Concluded from p. 31).

LENHER and Morgan (*Journ. Amer. Chem. Soc.*, 1900, xxii., 28), in their experiments on the conductivity of tellurium, found that alterations in the contact between the material and the electrode used caused the widest variation in their results. Indeed the best values they could get are very far from uniform.

In the year 1877 there appeared a second paper, by Siemens, devoted to a more detailed consideration of the action of light. He finds the greatest activity in the red region of the spectrum; concludes that there are too many disturbing influences in the measurements to make it possible to find any fixed relationship between the light intensity and the resulting change of conductivity; and, finally, presents some detailed experiments on the effect of continued illumination upon the cells.

At the same time, Forssmann announced the results of some extended experiments upon the action of light of different colours. His first results go to show a maximum effect in the red and yellow, a minimum in the green; but he found indications later on, that even invisible rays may produce an effect. For instance, lamp-light which had passed through a solution of chromic chloride had a larger effect than the direct light itself, although the colour of the chromic chloride was so intense that it was opaque to the eye even in direct sunlight. Other salt solutions were studied as well, but no general conclusions could be drawn from the results.

In the following year (1878), Sabine published a paper on "Some Electrical Experiments with Crystallised Selenium," in which he brings out very clearly the enormous importance of the junctions in the behaviour of selenium cells. "A large portion of the observed resistance of a so-called selenium resistance may, and frequently does, reside in the junctions and not in the selenium." The same is shown to apply also to the alterations brought about by inversion of the current. Light and heat appear from his experiments to act in the same way upon the conductivity of selenium surfaces; and, finally, the alterations brought about by these means are shown to be probably in the nature of an actual change in resistance, rather than, as some investigators have supposed, an electromotive force set up in the selenium in the same direction as the battery current.

Alexander Graham Bell, in 1880, presented an account of his practical applications of the selenium cell in the construction of the photophone. He found that "brass, although chemically acted upon by the selenium, forms an excellent and convenient material. Indeed, we are inclined to believe that the chemical action between the brass and the selenium has contributed to the low resistance of our cells by forming an intimate bond of union between the selenium and the brass." There is but little of theoretical interest in the paper except that Bell finds the long heating and slow cooling formerly recommended in the preparation of selenium cells to be unnecessary; this is probably because selenium acts more rapidly upon brass than upon platinum.

* From the *Journal of Physical Chemistry*, vol. iv., No. 6.

Obach (1880), found that phosphorescent light caused a change in the conductivity of selenium. The phosphorescent material used was of unknown composition, but being a commercial article was probably one of the alkaline earth sulphide preparations. Its action was relatively slight, yet distinct. Strangely enough, it was entirely cut off by the interposition of red or yellow glass, while blue glass transmitted six-sevenths of the original effect.

There is through these years a large amount of literature on the applications of selenium cells, scattered through such journals as *Nature*, the *Journal of the Society of Telegraph Engineers*, &c. I have been at no special pains to collect references to such letters and short communications except in the cases where some fact of theoretical importance has been brought out. The best general account of this side of the subject will be found in Bell's paper cited above.

Kalischer's article in 1881 under the title of "Photophone without Battery," describes his attempts to produce a photophone in which the current was supplied by the electromotive force of the selenium preparation itself under illumination.

Moser (1881), records some very interesting observations on the nature of the contact between selenium and metals:—"On a copper plate I melted amorphous selenium, and put on it a second metal plate of zinc or copper. Then I heated gradually so that the selenium became crystalline; and I then annealed it. Whilst the amorphous selenium adheres very well to the metal plates, these cells proved very brittle when the selenium was crystalline. The selenium always split off from the copper plate. . . . Every lamina which split off was on the upper side light grey, and on the lower side blue-black, not brilliant, but dull. In the same way, the copper plate had now a similar dull blue-black covering. This blue black body is cuprous selenide. . . . This experiment shows that between the copper and the selenium, or rather the cuprous selenide, there is only a slight and imperfect contact."

The view advanced by Moser that "selenium is heated by light," and that the changes in its conductivity are produced through the expansion of the mass of selenium and consequent tightening of the contacts, was disproved by Shelford Bidwell in 1883. We have seen too that experiments made some years previous had shown that the peculiar action of selenium cells could not be explained as a heating effect.

Fritts, in 1883, described the preparation of selenium cells of hitherto unattained sensitiveness and of very low resistance. One of them showed fifteen times as high a resistance in the dark as it had in ordinary diffused daylight of the room. He finds that the best metals to use are "brass, zinc, or iron or copper thinly coated with tin." (Apparently only the copper was tin-plated). The properties of these cells are in other respects also quite unusual. It was found, for example, that the kind of battery has a great deal to do with the result; thus, some cells which were light sensitive when operated with a Leclanché battery gave no results at all with a bichromate battery. The effect of rapidly alternating currents was in some cases to reduce the resistance of a cell from many thousands of ohms to almost nothing; in other cases to raise it from next to nothing up among the thousands. These extremely variable results are left quite without explanation.

Fritts describes, in the latter part of his paper, the preparation of a new modification of selenium. The method of preparation is only imperfectly indicated, but seems to me by prolonged heating of selenium on a brass plate (to what temperature ?), and then gradually cooling, under pressure. "The plates so made have portions which are transparent, situated apparently where the temperature was highest. The remaining portions of the plates are black and red, interspersed with grey. Thus, upon one plate may be seen selenium in four different states or colours. . . . A small portion of the trans-

parent selenium having, perhaps, one-half square inch of surface, had a resistance of only three ohms. It was found to be affected by light very little, if at all."

This transparent film which he considers as a new modification of the element, was perhaps in reality a film of fused selenide; or, it may have been a thin film of vitreous selenium, which is almost colourless in very thin layers. In the latter case we must assume an experimental error in the measurement of its resistance.

Selenide of zinc is described as a reddish-yellow substance. It is possible that this may have been the transparent material observed by Fritts.

In 1884, Bidwell, in a short article on the resistance of sulphur and selenium cells, showed that sulphur also gives light-sensitive cells when it contains sulphide of silver, and that selenium which has never come into contact with a metal possesses a resistance enormously higher than the ordinary material in the selenium cell. In a longer article, in 1885, the same author puts forward the hypothesis that the peculiarities of the selenium cell are really due to the presence of selenides. If this is the case, then the conduction may very well be electrolytic, and would lead to the deposition of free selenium at one electrode, and of the metal at the other. A change of this kind in the nature of the contacts might easily give all the remarkable irregularities in the behaviour of selenium cells which have been recorded as the results of (1) a steady passage of the current, and (2) a reversal of its direction.

Kalischer (1887), studied the conditions under which the selenium cell becomes, as that author says, photoelectromotive. The cells have the ordinary form, but are constructed of two different metals, the selenium forming a connection between them. Copper and zinc were found to be a very efficient pair. They have, as a rule, a comparatively high resistance. "Besides the copper-zinc combination, I have used also copper-brass, zinc-brass, and copper platinum. In all of these, the direction of the current which is called forth by light is the same as in the ordinary galvanic elements. Thus, for instance, from zinc through the selenium to the copper." Nevertheless, the same results may be obtained, using only one metal for the electrodes, though the current is less marked in this case. With lapse of time, the cells lose their power, and this loss is coupled with a decrease in resistance.

It is in this direction that most of the more recent work on selenium cells has been done. Thus, v. Uljanin (1888) and Righi (1888) have both made important contributions to our knowledge of the electromotive force of selenium in the light.

Righi (1889), finds further that a selenium cell constructed with electrodes of different metals shows an electromotive force even in the dark.

Hesehus (1884), in a purely theoretical paper, discusses the different explanations which have been suggested for the abnormal conductivity of selenium, and favours the assumption of two metallic forms of the element—Siemens's idea.

Bidwell, in 1891, carries on the argument in favour of the theory that the behaviour of selenium cells is due to selenides. He shows that the "annealing" of the cell, which has almost always been regarded as absolutely necessary to the production of good light-sensitive cells, would in reality lead to the formation of a film of selenide at the junction. The deterioration of the cells with age he attributes to the gradual thickening of the layers of selenide at the expense of the free, badly-conducting selenium, and thus the resistance of the cells slowly falls. "At length the layers of selenide become so thick that the coatings upon the two wires actually meet and touch each other. Thereupon the cell is short-circuited; its resistance no longer depends upon the selenium, but upon the metallic selenide, which is a good conductor."

The deposition of free selenium upon the electrode in the form of a covering of red tufts was shown experimentally. This material is amorphous selenium, which, as we know, is a good insulator; hence the alterations in conductivity produced by continued use of the cell may well be large.

Since the appearance of this paper of Bidwell's no great addition has been made to the knowledge of the subject. Siemens, in his important paper, advanced the theory of a second form of metallic selenium, produced at 200°. That is the only good explanation, other than Bidwell's, which has been offered. Now we have seen in the other sections of this paper that it has been quite impossible to get any direct evidence of the formation of a new modification of selenium at higher temperatures. Furthermore, even granting its existence, there are still very many of the recorded observations which cannot be explained satisfactorily on that ground. The hypothesis of Bidwell gives much more hope of an ultimate clearing up of all the known facts. We have seen that selenides are undoubtedly produced when selenium is heated in contact with metals; that those metals—copper and brass—which are the most efficient in yielding sensitive cells, are among the ones most readily attacked. Hence the presence of selenides is certain. Bidwell has shown that there is a deposition of amorphous selenium at the anode, which would hardly be the case if the conduction were not really electrolytic. This deposition may well be the cause of the extraordinary differences observed on the reversal of the current, &c. Selenides are known to be good conductors; unfortunately, the action of light upon them has not been studied; but the fact that sulphur which contains silver sulphide displays the light-sensitiveness of a selenium cell supplies an argument by analogy of considerable force.

Furthermore, Bidwell found that a silver leaf placed upon glass and painted over with a solution of sulphur in carbon disulphide, if only partly shaded from the light, became, after fifteen minutes, dark brown in the illuminated part, while remaining whitish-yellow where shaded. It may be mentioned here that Schuller (1883), found that when selenium is distilled there is a residue left containing copper and lead; this indicates that the commercial material is probably always more or less contaminated with metals.

It has recently been announced (1900), by Perreau that the resistance of selenium cells is reduced by X-rays, in the same way as by light.

So much of the time spent in the study of selenium cells has been devoted to the devising of instruments which have in the end proved inefficient that, in spite of the large literature of the subject, very few really scientific observations are on record. By beginning now with a methodical study of the behaviour of selenides, and of selenium and selenide mixtures of known composition, there is every hope that a conclusion might be reached which would set the whole matter on a firm basis, and supply moreover an interesting chapter on the action of light on chemical compounds.

11. *Coefficient of Expansion.*

Fizeau (1869), gives the value for the linear coefficient of expansion for vitreous selenium as 0·00003368. It is to be inferred that the experiment covered a range of temperature from 10° to 80°, and the value given above represents a mean result for 40—50°.

Spring (1881), made a determination of the cubical expansion of selenium in the crystalline (metallic) form; the results are given below; the first series refers to the powdered crystals; for the second, these were subjected to a pressure of 6000 atmospheres, to get rid of air cavities. s is the specific gravity, β the mean coefficient of expansion from 0° to $t°$.

	t	0°	20°	40°	60°	80°	100°
I.	s	4·7312	4·7176	4·7010	4·6826	4·6623	4·6396
	$\beta.10^7$	—	1478	1635	1743	1857	1981
II.	s	4·7994	4·7869	4·7699	4·7526	4·7351	4·7167
	$\beta.10^7$	—	1307	1539	1644	1803	1751

It will be noticed that the specific gravity in each of these cases is somewhat less than the value to which the best of the other determinations have led. Spring's method was that of the weight thermometer filled with water; hence it would not be surprising if the material contained noticeable air cavities; this would explain the higher results for the uncompressed selenium.

VI. General Properties of the Element.

1. *Atomic Weight.*

The first determinations are those of Berzelius (1818), and his results have only been confirmed by the latest and most accurate experiments. He found that 1 grm. of selenium gave, when treated with chlorine, 2·79 grms. of $SeCl_4$. This gives the atomic weight as 79·2 (Cl = 35.45). As a control experiment the chloride was transformed into the acid H_2SeO_3, and the hydrochloric acid thus liberated determined by silver nitrate. The chloride obtained from 1 grm. selenium yielded, in this way, 7·2285 grms. silver chloride, from which we calculate the value 79·35.

Berzelius did not, as Ostwald (*Lehrbuch*, i., 106) states, lay the greater emphasis on the first value; on the contrary, he gives as the most probable result, the mean of the two, but he does not state that of two such double determinations which he made he considers the first as the better, because it was made with the larger quantity of material. By another method he found that 1·888 grms. of silver selenide, Ag_2Se, yielded 1·844 grms. of silver chloride, from which the atomic weight is found to be 77·98 (Ag = 107·9).

The analysis of barium selenate quoted by Ostwald was not made as a determination of atomic weight. The same remark applies to the work of Mitscherlich and Nitzsch, who made an analysis of selenic acid,

The next atomic weight determination is therefore that of Sacc (1847); in this case also several analyses of salts were made, which were recognised by that author as being unsuitable for atomic weight determinations. The methods upon which he laid stress were:—

(1). The reduction of selenium dioxide by ammonium bisulphite and hydrochloric acid. This method yielded the results 78·3—78·2—79 (O = 16), and

(2). The reduction of barium selenite by the same reagents, and weighing the mixture of barium sulphate and selenium which is precipitated. This is a less accurate method, and gave, as the mean of three determinations, about 78·6.

Erdmann and Marchand (1849), analysed mercuric selenide, and found that it contains 71·726—71·731—71·741 per cent of mercury. These values give as the atomic weight 78·96, 78·96, 78·93.

Dumas (1859), made a series of determinations in which he converted known weights of selenium into the chloride $SeCl_4$. His results vary from 79·2 to 79·66, and give as a mean value 79·46. As pointed out by Meyer and Seubert, Dumas has recorded in his article, in every case, the increase of weight as if it were the total final weight—*i.e.*, what he calls the weight of chloride is really the weight of the absorbed chlorine.

Petterson and Ekman (1876), used two different methods:—

(1). By weighing the silver obtained from silver selenite by heating, they obtained seven values varying between 78·90 and 79·18, and giving in the mean 79·01.

(2). By reducing weighed quantities of selenious acid by means of sulphur dioxide, and determining the weight of the selenium precipitated, they found in five results a variation from 79·06 to 79·10; in the mean, 79·08.

They consider the second method the more trustworthy, and give the value 79·08 as representing most nearly the true atomic weight.

Finally, Lenher (1898), made a very careful study of the problem by the following methods:—

(1). Silver selenite was converted into silver chloride; in this way, eleven results were obtained varying from 79·263 to 79·326.

(2). The silver chloride so obtained was then reduced in the case of eight of these, and gave values between 79·277 and 79·369.

(3). A weighed quantity of the bromide $(NH_4)_2SeBr_6$ was reduced by hydroxylamine, and the resultant selenium weighed. Eight determinations gave values between 79·226 and 79·367. Lenher's mean values are:—

From silver chloride	79·329 (eleven results).
From metallic silver	79·329 (eight results).
From bromide	79·285 ,,

The general mean is therefore 79·31.

The values given in the most recent standard tables of atomic weights are as follows:—

German Chemical Society (*Ber.*, 1898, xxxi., 2761) ..	79·1
F. W. Clarke (*J. Am. Chem. Soc.*, 1900, xxii., 70) ..	79·2
Richards (table for 1899, quoted by Clarke)	79·2

2. *Boiling-point.*

Carnelley and Williams (1879), found a value lying between 676° and 683°. Their method of determining the temperatures was by using substances of high melting-point previously determined, and exposing them to the vapour of the boiling liquid.

Troost (1882), found the boiling-point to be at about 665° under a pressure of 760 m.m. The temperature was measured with a form of air thermometer.

3. *Vapour-density.*

Sainte-Claire Deville and Troost (1863), in their researches on vapour-density at high temperatures, determined that of selenium at 1420°, and found it to be 5·68, corresponding to a molecular weight of 164·0°. The values for the molecular weight at lower temperatures are:

	Mol. wt.
At 1040°	184
At 860°	222

4. *Spectrum.*

In 1863 Werther published a note on the similarity between the spectra of selenium and lead. Ditte (1871), made a comparative study of the spectra of sulphur, selenium, and tellurium. He found well marked yellowish-green lines in the selenium spectrum toward the E line, and also two brilliant blue bands near to and to the left of the G line.

The work of Salet as well as that of Plücker and Hittorf is summarised in the report of a special committee of the British Association for the Advancement of Science (1884). The tables there given are too long to be quoted here.

5. *Absorption Spectrum.*

Gernez (1872), records that the vapour of selenium absorbs the rays of the spectrum up to about the C line; but at higher temperatures there is extinction in the blue and violet.

6. *Capillarity Constant.*

Quincke (1868), determined the capillarity constant of selenium by the method of drops, and found—

$$a = 7{\cdot}180 \text{ m.g. for } 2r = 1 \text{ m.m.}$$

VII. Conclusion.

In conclusion, I desire to express my sincerest thanks to Professor W. D. Bancroft, in whose laboratory this work was carried on; I am indebted to him not only for suggesting the subject of the investigation to me, but also for his continued interest and timely suggestions while it has been in progress.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING DECEMBER 31ST, 1900.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, January 10th, 1901.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 192 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Dec. 1st to Dec. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 192 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during December shows a slight excess for the first time since the month of August. The actual rainfall has been 2·20 inches, the average for the month is 2·10 inches, making an excess of 0·10 inch; this reduces the total deficit for the year to 3·12 inches, or 12·1 per cent on the thirty years' average, as will be seen by the following table:—

TABLE A.—*Rainfall in Inches at Oxford, Month by Month, during the Year* 1900.

	Actual fall. Inches.	Mean of 30 years. Inches.	Difference from the mean. Inch.	Inch.
January ..	2·30	2·16	—	+0·14
February ..	4·23	1·76	—	+2·47
March ..	0·50	1·50	−1·00	—
April	0·89	1·66	−0·77	—
May	1·33	1·83	−0·50	—
June	2·73	2·11	—	+0·62
July	0·88	2·68	−1·80	—
August ..	3·13	2·32	—	+0·81
September..	0·41	2·43	−2·02	—
October ..	2·35	2·75	−0·40	—
November..	1·65	2·42	−0·77	—
December..	2·20	2·10	—	+0·10
	22·60	25·72	−7·26	+4·14

TABLE B.—*Table showing Average Monthly Bacterial Variations during the Year.*

Month.	Thames, unfiltered.	Thames-derived Companies, filtered.	New River, unfiltered.	New River, filtered.	River Lea, unfiltered.	River Lea (East London), filtered.	
January	2235	22	621	10	694	7	
February	8086	66	682	18	692	13	
March..	1694	18	282	8	426	5	
April	955	10	245	4	324	5	
May	932	19	104	6	283	6	
June	1677	9	95	8	221	11	
	2596	24	338	9	440	8	Mean of 1st 6 months.
July	1338	25	299	11	450	19	
August	2349	9	94	4	138	8	
September	4332	14	121	10	158	13	
October	1441	26	184	10	212	15	
November	1173	17	179	5	262	5	
December	1548	15	326	10	397	10	
	2030	18	200	8	269	12	Mean of 2nd 6 months.
	2313	21	269	9	354	10	Mean of 12 months.

TABLE C.—*Average Number of Microbes in the Filtered London Waters for the Past Four Years.*

	Thames-derived Companies.	New River.	River Lea.
1897	46	32	62
1898	34	30	25
1899	2	15	20
1900	2	9	10

TABLE D.—1900.—*Averages of the Supplies derived from the River Thames.*

	Common salt per gallon. Means.	Nitric acid per gallon. Means.	Hardness. Degrees. Means.	Oxygen required per gallon. Means.	Organic carbon per gallon. Means.	Organic carbon per gallon. Maxima.	Colour. Brown : Blue. Means.
January	2·389	1·059	16·04	0·060	0·185	0·257	27·5 : 20
February	2·350	1·063	15·56	0·064	0·190	0·255	29·0 : 20
March	2·075	1·147	16·13	0·063	0·191	0·298	29·0 : 20
April	2·132	0·915	15·78	0·036	0·114	0·145	21·5 : 20
May	2·080	0·807	14·99	0·028	0·086	0·105	12·9 : 20
June	2·099	0·916	14 55	0·033	0·085	0·100	11·4 : 20
July	2·128	0·746	13·30	0·038	0·069	0·091	14·0 : 20
August	2·078	0·616	13·06	0·035	0·079	0·096	14·0 : 20
September	2·163	0·661	13·52	0·030	0·068	0·088	12·9 : 20
October	2·216	0·769	13·79	0·029	0·077	0·225	12·5 : 20
November	2·261	0·866	15·20	0·032	0·085	0·111	12·3 : 20
December	2·360	0·847	15·55	0·045	0·110	0·134	13·7 : 20

Our bacteriological examinations of 498 samples have given the results recorded in the following table; we have also examined 36 other samples, from special standpipes, &c., making a total of 534 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 24 samples) ..	326
New River, filtered (mean of 126 samples) ..	10
Thames, unfiltered (mean of 24 samples) ..	1548
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 264 samples)	15
Ditto ditto .. .. highest	194
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 24 samples) ..	397
River Lea, from the East London Company's clear-water wells (mean of 36 samples) ..	10

Of the 426 samples of the filtered water supplied to London, examined bacteriologically during the past month, only six samples, or 1·4 per cent of the whole number of samples examined, contained more than 100 microbes per c.c.

During the past year we have examined 6731 samples of London waters bacteriologically, as compared with 4792, 3500, and 3249 respectively in the three previous years. We have also made 2478 chemical analyses of London waters throughout this period, making a total of 9209 samples examined during the year.

The results of the filtration of the London waters are given in Tables B, C, and D.

Table B shows that during the first six months the Thames-derived Companies' clear-water wells contained on the average 24 bacteria per c.c., while the New River and River Lea supplies contained respectively 9 and 8. During the second six months, the number of bacteria in the waters from the three were respectively 18, 8, and 12.

From Table C it will be seen that from 1897, when the bacteriological condition of the London water supply was highly satisfactory, being much below 100 microbes per c.c., there has been, nevertheless, a steady improvement with each succeeding year. This improvement is not confined merely to the Thames-derived waters, but is more apparent in the New River and the Lea supply. It is interesting to note that in the year 1900, as compared with the year 1897, the average microbic purity has been raised about 55 per cent in the Thames derived waters, while in the New River it has been raised some 70 per cent, and in the case of the Lea, nearly 85 per cent. We attribute these extraordinary results to the increased knowledge of the scientific treatment of the filter beds, and to the fact that, as bacteriological examinations of each of the Companies' supplies are made every day, we are in a position to communicate immediately to the engineers in charge any retrograde change that may be taking place in the efficiency of the filtration.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

A Compound of Fluoride of Silver and Fluoride of Ammonium.—B. Grützner.—The author makes use of commercial NH_4F. Into a solution of this salt, prepared in the cold, and as concentrated as possible, he drops Ag_2O freshly precipitated by NaOH free from the chloride, so long as this oxide is dissolved. On cooling the solution to 0°, crystalline needles are deposited (2 grms. for each 50 grms. of Ag_2O); these are washed with distilled water, and dried with blotting-paper, while being kept cool and away from the light. Their analysis shows that they consist of the double salt $2NH_4F+AgF+H_2O$. The property of AgCl of being slightly soluble in concentrated NH_4Cl thus reappears with AgF, which is much more easily soluble, forming the above double salt.—*Arch. de Pharm.*, vol. ccxxxviii., p. 1.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 20th, 1900.

Professor THORPE, C.B., F.R.S., President, in the Chair.

(Concluded from p. 34).

176. "*The Action of Ethylene Dibromide on Xylidine and Pseudocumidine.*" By ALFRED SENIER and WILLIAM GOODWIN.

The reaction between ethylene dibromide and aniline originally studied by Hofmann, and extended to homologues of both compounds by subsequent observers, has been applied to xylidine and pseudocumidine. Dixylylethylenediamine and dicumylethylenediamine were obtained, together with their related piperazines. From the diamines, derivatives were prepared homologous with those obtained by Mills (*Trans.*, 1900, lxxvii., 1020). *Dixylylethylenediamine*, $C_2H_4(NHC_6H_3Me_2)_2$, white feathery crystals, m. p. 74—75°. *Dixylylethylenediamine nitrate*, $C_2H_4(NHC_6H_3Me_2)_2(HNO_3)_2$, m. p. 166°. *Dixylylethylenediamine platinichloride*, $C_2H_4(NHC_6H_3Me_2)_2(HCl)_2PtCl_4$, bright yellow crystals. *Dixylylethylenediamine mercurichloride*, $C_2H_4(NHC_6H_3Me_2)_2HgCl_2$, pale yellow crystals, m. p. about 118°. *Tetranitrodixylylethylenediamine* $C_2H_4[NHC_6H(NO_2)_2Me_2]_2$, pale yellow crystals, m. p. 220°. An *isomeride*, m. p. 52—53°. *Mononitrodixylylethylenediamine*, m. p. 152—154°, and a *trinitro*-derivative, m. p. 191—192°. *Dixylylpiperazine*,—

$$Me_2H_3C_6N(C_2H_4)_2NC_6H_3Me_2,$$

consists of shining white leaflets, m. p. 151°. *Dipseudocumylethylenediamine*, $C_2H_4(NHC_6H_2Me_3)_2$, brilliant colourless needles, m. p. 168°. *Dipseudocumylethylenediamine nitrate*, $C_2H_4(NHC_6H_2Me_3)_2(HNO_3)_2$, colourless needles, m. p. 154°. *Dipseudocumylethylenediamine platinichloride*, $C_2H_4(NHC_6H_2Me_3)_2(HCl)_2PtCl_4$, buff-coloured powder. *Dipseudocumylethylenediamine mercurichloride* $C_2H_4(NHC_6H_2Me_3)_2HgCl_2$, crystals melting at 150°. *Dinitrodipseudocumylethylenediamine*, $C_2H_4[NHC_6H(NO)Me_3]_2$, yellow powder, m. p. 97—98°; an *isomeride*, m. p. 49—50°. *Dipseudocumylpiperazine*, $Me_3H_2C_6N(C_2H_4)_2NC_6H_2Me_3$, colourless needles, m. p. 148—150°.

177. "*The Action of Phenyl Carbimide on Diphenyl-, Dialphyl-, and Dinaphthyl-diamines.*" By ALFRED SENIER and WILLIAM GOODWIN.

When the two ethylenediamines described in the preceding abstract were treated with phenyl carbimide an interesting reaction resulting in the formation of ethylenediamines of the type $C_2H_4(NR'\cdot CO\cdot NHPh)_2$ was brought to light. These diamines are analogous to the ethylenediamine of Volhard (*Ann.*, 1861, cxix., 349), and to the trimethylene carbanilide of Hanssen (*Ber.*, 1887, xx., 783). The reaction is shown to be a general one by the formation of the following homologues:—*Dicarbanilido-diphenylethylenediamine*, $C_2H_4NPh\cdot CO\cdot NHPh)_2$, m. p. 220°. *Dicarbanilido-ditolyl ethylenediamines*,—

$$C_2H_4(NC_6H_4Me\cdot CO\cdot NHPh)_2.$$

The *ortho*-derivative melts at 195—196°, the *meta*- at 181·5°, and the *para*- at 186°. *Dicarbanilido-dixylylethylenediamine*, $C_2H_4(NC_6H_3Me_2\cdot CO\cdot NHPh)_2$, melts at 167°. *Dicarbanilido-dipseudocumylethylenediamine*, $C_2H_4(NC_6H_2Me_3\cdot CO\cdot NHPh)_2$, m. p. 191°. *Monocarbanilidodi-α-naphthylethylenediamine*,—

$$C_2H_4(NHC_{10}H_7)(NC_{10}H_7\cdot CO\cdot NHPh),$$

m. p. 266°.

178. "*Note on the Action of Nitrous Acid on β-nitroso-α-naphthylamine.*" By ARTHUR HARDEN and J. OKELL.

When β-nitroso-α-naphthylamine is treated in alcoholic solution with potassium nitrite and hydrochloric acid, it yields a potassium salt, $C_{10}H_6O_2N_3K$, which crystallises

in reddish-coloured needles, and decomposes vigorously at 250°. A different salt, described in a previous paper (*Ann.*, 1889, cclv., 148), was obtained by this reaction, which had the formula $C_{10}H_6O_4N_4KH$, and crystallised with $1\frac{1}{2}H_2O$, but on repeating the experiments the exact conditions necessary for the formation of this salt could not be ascertained, and the simpler salt, which differs from it by the elements of nitrous acid, was always obtained. Sodium nitrite yields the corresponding salt, $C_{10}H_6O_2N_3Na$. These salts behave towards acids in a manner similar to that already described, yielding, with hydrochloric acid and stannous chloride, a compound, $C_{10}H_6N_3{\cdot}OH$, which probably has the constitution of an imidazole,—

$$C_{10}H_6\begin{cases}\text{———}N\\ N(OH)\end{cases}\!\!>\!\!N$$

(compare Zincke and Schwarz, *Ann.*, 1900, cccxi., 329). This substance crystallises with $1H_2O$, decomposes violently at 222°, and acts as an acid, yielding crystalline salts of sodium, potassium, and barium. The silver salt has the formula $C_{10}H_6{\cdot}N_3OAg$, and not that previously ascribed to it. The acetate melts at 109°, and the silver salt yields colourless, crystalline derivatives when heated with methyl and ethyl iodides.

The isomeric *α*-nitroso-*β*-naphthylamine behaves towards nitrous acid in a similar manner, yielding a potassium salt, $C_{10}H_6N_3O_2K+H_2O$, which, with hydrochloric acid and stannous chloride, gives a compound, $C_{10}H_6N_3{\cdot}OH$, which decomposes at 245°, and is isomeric with that described above, which it closely resembles in its properties.

179. "1 : 2 : 4-*Metaxylidine-6-sulphonic Acid.*" By HENRY E. ARMSTRONG and L. P. WILSON.

One of the authors has on previous occasions discussed the conditions under which either ortho- or para- or meta derivatives are formed from benzenoid amines, and has argued that meta-derivatives are produced by the direct attack of the benzene nucleus, whilst ortho- and para compounds are formed by a process of isomeric change in which the radicle is transferred from the nitrogen into the nucleus. An opportunity of further testing this generalisation is afforded by 1 : 2 : 4-metaxylidine. When sulphonated by an excess of fuming acid, this is readily converted into the 5-sulphonic acid, the only metaxylidinesulphonic acid hitherto described; it was to be supposed that the 6-sulphonic acid would be readily obtained on heating the sulphate, and this proves to be the case.

When metaxylidine is mixed with a single molecular proportion of 100 per cent sulphuric acid, and the mixture heated at 185° to 195° during six hours, the product then dissolved in water, and the solution neutralised with potassium carbonate, 90 per cent of the theoretical amount of *potassium*-1 : 2 : 4 : 6-m-*xylidinesulphonate*, $C_6H_2(CH_3)_2(NH_2){\cdot}SO_3K$, is obtained. *Potassium*-1 : 2 : 4 : 6-*aceto*-m-*xylidinesulphonate*, $C_6H_2NH(CH_3)_2Ac{\cdot}SO_3K$, is obtained by heating the potassium sulphonate with acetic anhydride. It is a colourless substance crystallising from alcohol in spindle-shaped needles. On adding bromine to its solution in water, the sulphonic group is not affected, although it is easily displaced from the unacetylated acid.

Potassium-1 : 3 : 5-m-*xylenesulphonate*,—

$$C_6H_3(CH_3)_2{\cdot}SO_3K,\tfrac{1}{2}H_2O,$$

is obtained from the 1 : 2 : 4 : 6-*m*-xylidinesulphonate by diazotising, and then boiling with alcohol, or by means of the hydrazine; it crystallises from water in thin, colourless, lustrous leaves, and is nearly insoluble in alcohol. On fusing this salt with potash, it is converted into 1 : 3 : 5-*m*-xylenol, m. p. 65°. *Barium* 1 : 3 : 5-m-*xylenesulphonate*, $(C_6H_3Me_2{\cdot}SO_3)_2Ba,2H_2O$, crystallises from water in fine, colourless leaves. 1 : 3 : 5-m-*Xylenesulphonic acid* crystallises from water in thin, transparent flattened needles. 1 : 3 : 5-m-*Xylenesulphochloride*, $C_6H_3(CH_3)_2{\cdot}SO_2Cl$, crystallises from light petroleum and benzene in needles, and from chloroform in massive crystals; m. p. 94°. 1 : 3 : 5-m-*Xylenesulphobromide*, $C_6H_3(CH_3)_2{\cdot}SO_3Br$, resembles the sulphochloride in crystalline behaviour; m. p. 92—93°. 1 : 3 : 5-m-*Xylenesulphonamide*, $C_6H_3(CH_3)_2{\cdot}SO_2NH_2$, crystallises from water in very lustrous, colourless flakes, and from benzene in very fine needles; m. p. 134°. 1 : 3 : 5-m-*Xylenesulphanilide*, $C_6H_3(CH_3)_2{\cdot}SO_2{\cdot}NH{\cdot}C_6H_5$, crystallises from alcohol in large, monosymmetric crystals; m. p. 119°.

$$a : b : c = 0{\cdot}8718 : 1 : 0{\cdot}7341. \quad \beta = 110°58'.$$

1 : 3 : 5-m-*Xylenesulpho*-p-*toluidide*,—

$$C_6H_3(CH_3)_2{\cdot}SO_2NH{\cdot}C_6H_4{\cdot}CH_3.$$

crystallises from alcohol in monosymmetric crystals resembling the anilide; m. p. 121—122°.

$$a : b : c = 1{\cdot}18195 : 1 : 0{\cdot}9380. \quad \beta = 101°7'.$$

180. "*The Preparation of Acetylchloraminobenzene and Related Compounds.*" By F. D. CHATTAWAY and K. J. P. ORTON.

The authors reply to Armstrong's recent criticism of the authors' work. The statements which he calls in question are proved to be correct, and details are given of the method of preparing acetylchloraminobenzene. It is also shown that acetylchloramino-2 : 4-dichlorobenzene can be obtained by the direct action of chlorine on acetanilide.

CORRESPONDENCE.

DIVISION OF NITROGEN IN CHEMICAL MANURE COMPOUNDS.

To the Editor of the Chemical News.

SIR,—Having been engaged in connection with the manufacture of artificial fertilisers two or three years ago, I have also been much interested in that phase of manuring which Mr. J. Ostersetzer emphasises (CHEM. NEWS, lxxxiii., p. 3).

My attention was first drawn to the matter by the success of certain fertilisers of low percentage, as compared to more concentrated ones, which though well-balanced as regards their essential constituents, and with these constituents thoroughly well incorporated, gave poorer results than the low percentage manures, each being applied in proportional quantities.

These differences, though occurring in the hands of practical gardeners, &c., could only be explained as being due to the improper dilution of the concentrated fertiliser by mixing with dry earth or other material, and I came to the conclusion that this dilution was effective when thoroughly mixed, as would occur at a works, in not only separating the particles of phosphate, &c., one from another, but in still further disintegrating such particles, thus causing a much better distribution throughout the mass.

With this in view I tried a few experiments with a mixture of sand and gypsum, containing a maximum of 2 per cent of sulphate of ammonia, distributed by thoroughly mixing in a solution of the sulphate, thus ensuring fineness of division in, I should think, as perfect a manner as is possible.

The result of the use of such a mixture was surprising, for, tested against well compounded manures of the usual kind, the nitrogen was found to be almost four times as effective in producing growth of plants upon which it was tried.

I have been much confirmed in the importance that is to be attached to finenes of division, by the results obtained by a certain patented manure a few years ago. This contained only about 2 per cent of ammonia as sulphate, no phosphates, and only a trace of potash; yet its results, which I have seen for myself, certainly sur-

passed many fertilisers of a much higher percentage in ammonia, &c., when these latter have been applied in the manner usually adopted by the average gardener, that is by sprinkling the surface of the soil with the compound, or else imperfectly mixing with a little dry earth.

In the case of the patented manure mentioned nothing was claimed by the makers for the action of the ammonia, but its whole effect was put down to special properties which it was said to possess in the way of supplying silica in an assimilable form. On examination, however, I concluded that its merit depended entirely upon the ammonia, and this being so low in percentage, its efficiency must be due to its fine state of division, and this I consider proved by experiments with the mixture of sand, gypsum, and ammonia sulphate before mentioned.

In the case of compounds in which nitrogenous refuse matter is worked up by the aid of sulphuric acid, Mr. Ostersetzer has shown that part of the nitrogen present becomes converted into sulphate of ammonia, which becomes widely distributed throughout the mass by going into solution during the mixing in the excess of acid which is present in compounded manures of this class.

This gives a reason for the preference shown by many farmers for such manures; they give good results, and seem cheaper, though as a matter of fact they are generally sold at prices absurdly out of proportion to their value, reckoned on analysis. On the other hand, a concentrated form of fertiliser may give a comparatively poor reault, because the farmer must needs mix it with a diluent before he can spread it on his land, and this is too often done imperfectly, either through carelessness, ignorance, or lack of means.

If, however, the mixing were done on the farm in a proper manner, the concentrated forms would be the cheapest, as these being sold at prices more in accordance with the result of analysis, and as the source of ammonia must be inorganic in order to obtain a high percentage of ammonia, better value in this essential alone is assured. Added to this is the saving in cost of carriage.

If the farmer can succeed in making homogeneous mixings he may of course proceed to reap the full advantage of his skill, and do away with purchases of compounded fertilisers, mixing his own, or, still better, put his potash salts, phosphates, and nitrogenous material on the land in a well diluted condition at different seasons, and thus do his manuring in a truly rational manner. But until he can make a decent mixture the artificial manure manufacturer will still find customers among the agriculturalists.—I am, &c.

W. S. Lambert.

56 Leytonstone Road, Stratford, E.
January 16, 1901.

APPARATUS FOR STORING SOLUTIONS.

To the Editor of the Chemical News.

Sir,—The following is the description of an extremely simple apparatus which has all the perfections without having any of the obvious imperfections of the apparatus described by Mr. E. Dowzard in the Chemical News (vol. lxxxiii., p. 18):—

A cork in which two holes have been bored is fitted into the neck of the bottle in which the solution is to be stored; a funnel furnished with a tap, through which the solution may be returned to the bottle, is inserted in one hole, and a tube, also furnished with a tap, to allow air to flow in or out as the solution is run out or in, is inserted in the other; another tube having a tap through which the solution is run out, is fixed in a neck made low down at the side of the bottle. To prevent evaporation, &c., oil is poured on to the solution.—I am, &c.,

Nemo.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, del'Académie des Sciences. Vol. cxxxi., No. 27, December 31, 1900.

The Place of Indium in the Classification of the Elements.—C. Chabrié and E. Rengade.—The authors obtain double sulphates of indium and two well-defined alkaline metals, cæsium and rubidium. This fact, added to observations made by other chemists, seems to be sufficient to definitely include indium amongst the metals capable of giving sesquioxides. Apparently, also, the property of indium hydrate of being soluble in the alkalis, brings this metal nearer to aluminium than iron. It is worth remarking that indium acetylacetonate, so well-defined and beautifully crystalline, is not volatile and so cannot be used to determine the atomicity of indium. This latter fact brings indium nearer to iron and removes it from aluminium; the acetylacetonate of aluminium being volatile without decomposition.

Nitrate of Uranium.—Œchsner de Coninck.—The author determines the densities of several solutions of uranium nitrate in methyl alcohol—both commercial and pure—and in pure acetic acid of density 1·035. He examines the stability, with regard to diffused solar light, of the principal solutions of the same salt. He also measures the solubility of uranium nitrate in commercial methyl alcohol, in ethyl alcohol at 85°, in acetone purified from bisulphate, and in pure acetic acid.

Crystalline Form of Luteo-cobaltic Chlorosulphate and Chloroselenate.—T. Klobb.—During a preceding research, the author examined the form of crystals of luteo-cobaltic chlorosulphate, $(Co.6NH_3)SO_4.Cl+3H_2O$. The sharpness of the edges permitted excellent measurements to be taken. He now re-examines these, using more perfect crystals, and to confirm the conclusions drawn from the measurements of the above, he prepares luteo-cobaltic chloroselenate, $(Co.6NH_3)SeO_4.Cl+3H_2O$, a salt which is isomorphous with the above, and in which the mean value of $m\,m$ is 90° 4′ 30″. Very few substances have for their fundamental form a prism so near the quadratic prism. The derivative, $C_{22}H_{22}S_8$ has $m\,m$ of value 90° 8′, and the double tartrate of antimony and thallium is still less orthorhombic $m\,m$, having the value 90° 3′.

Osmosis of Liquids across a Membrane of Pig-bladder.—G. Flusin.—It has already been shown that the sense of velocity of osmosis of liquids across a vulcanised caoutchouc membrane depends on the capacity of absorption of the membrane for those liquids. The author endeavours to verify the fact, using methods and apparatus which he describes, that the same relation exists when a diaphragm such as pig-bladder is used. The numbers obtained show that the velocities of osmosis and the capacity of absorption vary in the same manner with pig-bladder as with vulcanised caoutchouc; the difference of affinity of the membrane for the two liquids with which it is in contact seems to determine the sense and intensity of the osmosis.

Indications of Organic Matter in certain Mineral Waters revealed by the Use of the Barium Hydrate Method.—F. Garrigou.—When barium hydrate is added to a mineral water, it precipitates all the metallic oxides contained in the water. This method of treatment enables a series of organic substances to be detected:—(1) Acids forming insoluble barium salts, perceived by the blackening of the barium precipitate on calcination. (2) The substances which barium hydrate leaves or sets free in the water, such as fatty materials and substances behaving as alkaloids; these can be extracted from the

water by means of benzine, petroleum ether, and chloroform. (3) An acid which is apparently freed from its compounds by sulphuric acid. (4) Substances which precipitate silver nitrate, in the same manner as the three halogens; these are probably the same as (3). (5) Finally, a neutral substance which remains in the last portions of the primitive liquid with the alkaline earths and the alkalis.

Presence of Methyl Alcohol in the Fermented Juice of various Fruits.—Jules Wolff.—Various authors have stated that methyl alcohol exists in the juice of certain plants previous to fermentation. This may be true to a certain degree, but the author shows that methyl alcohol appears during fermentation in the juice of a large number of fruits. He examines the juice of the following plants, and in all cases finds that the methyl alcohol has increased to a considerable extent:—Black currant, plum, cherry, apple, black and white grapes.

MISCELLANEOUS.

The Oxidising Value of the Alkaline Persulphates, and of Peroxide of Hydrogen.—B. Grutzner.—As_2O_5 is very well adapted for estimating the oxidising value of the persulphates:—

$$2K_2(SO_4)_2+As_2O_3+2H_2O=As_2O_5+2K_2SO_4+2H_2SO_4.$$

The operation is carried out warm in ordinary alkaline or ammoniacal solution. It is slower in acid solution. A $\frac{1}{10}$ N solution of As_2O_3 is used, the excess of which is estimated by a $\frac{1}{10}$ N solution of I. The valuation of H_2O_2 is made in the same manner, and gives results concordant with those furnished by the $KMnO_4$ method:—$As_2O_3+2H_2O_2=As_2O_5+2H_2O$. The author has not succeeded in titrating Na_2O_2 by the same method; the evolution of oxygen caused by this body is too rapid for the gas to combine integrally with the As_2O_3 at the moment of being set at liberty.—*Arch. de Pharm.*, ccxxxvii., p. 705.

Phosphide of Mercury and Compounds of Phosphonium.—A. Partheil and A. van Haaren.—The authors were unable to prepare phosphide of mercury, P_2Hg_3, by reacting with PH_3 on $HgCl_2$, either in the dry state or in solution; they were obliged to have recourse to Granger's method, which consists of reacting with P_2I_4 on Hg. By heating the P_2Hg_3 thus obtained with C_2H_5I, in sealed tubes to 160°, the body $P(C_2H_5)_4I.2HgI_2$ is obtained. This compound, treated with Ag_2O, gives the hydrate of tetrethylphosphonium:—

$$2[P(C_2H_5)_4I+2HgI_2]+5Ag_2O+H_2O=$$
$$=2P(C_2H_5)_4OH+10AgI+4HgO.$$

The base thus formed, when treated with HCl, gives the compound $P(C_2H_5)_4Cl$, which combines with $HgCl_2$, forming $P(C_2H_5)_4Cl.2HgCl_2$, and with $PtCl_4$ giving $[P(C_2H_5)_4Cl]_2PtCl_4$. The compounds obtained by this new method are identical with those prepared by the authors by the old process of A. W. Hofmann, C_2H_5I, reacting on $(C_2H_5)_3P$, &c. By heating CH_3I and P_2Hg_3 in sealed tubes to 150°, we obtain $P(CH_3)_4I.2HgI_2$, then successively $P(CH_3)_4Cl.HgCl_2$, $[P(CH_3)_4Cl]_2.PtCl_4$, and $P(CH_3)_4Cl.AuCl_3$.—*Arch. de Pharm.*, vol. ccxxxviii.

Some Properties of Gelatin.—C. Th. Mörner.—Gelatin may be washed for several weeks at the ordinary temperature with solutions of 0·2 to 0·5 per cent potash, without in any way losing its property of forming jelly, and without losing its sulphur. By this treatment the ash is reduced from 1·87 per cent to 0·13 or 0·16 per cent; but this is, however, independent of the washing with potash, as the same result can be obtained by simply washing with water. As many writers have found about 0·5 per cent of sulphur in gelatin, the author brings forward the hypothesis that there exist some gelatins containing one atom of sulphur and others containing two. Contrary to the statements of many writers, the Millon reaction has always been found to be positive. The author further shows that gelatin is really precipitable by acetic ferrocyanide, but that the precipitate is easily soluble in an excess of the reagent. Dilute solutions are precipitated more easily than concentrated ones. An increase of temperature, even to 30°, or the presence of neutral salts, diminishes or prevents the precipitation. The property of jellifying does not diminish with the increase of ash; this is contrary to the assertions of Nasse. The author contests the reality of the saline digestion, described by Dastre and Floresco (*Arch. de Physiol.*, xxvii., 701). The presence of neutral salts interferes with jellification, but digestion with salts in no way modifies the gelatin.—*Zeit. Phys. Chim.*, vol. xxviii., p. 471.

Action of Aluminium Amalgam on the Alcohols, Alcoholates of Aluminium, their Properties and Reactions.—V. Tistchenko.—The author has studied the action of aluminium amalgam on the various primary, secondary, and tertiary alcohols: all univalent alcohols are able to react on aluminium amalgam, giving alcoholates, $Al(OR)_3$; the essential condition of the reaction is that both the alcohol and the amalgam must be entirely free from water; the speed and ease of the formation, and of the separation of the alcoholates, depend on the nature of the alcohols; as a general rule, the primary alcohols react more easily than the secondary alcohols, and these more readily than the tertiary. The physical properties of the principal alcoholates obtained have already been described; it may, however, be remarked that the tendency to crystallise is only slightly remarked in the alcoholates of the normal primary alcohols, but it becomes more and more apparent as the number of molecules of CH_2 increases; the aluminates of the isobutyric and isopropylic alcohols, of trimethyl carbinol, and of dimethylethyl carbinol, can be obtained, however, in fairly large crystals, from their solutions in benzene or toluene. The molecular weight of the alcoholates has not been established by their vapour density, though many of them are volatile without decomposition; but the cryoscopic method indicates the general formula $Al(OR)_3$.—*Journ. Soc. Phys. Chim. R.*, xxxi., p. 694.

MEETINGS FOR THE WEEK.

Monday, 28th.—Society of Arts, 8. (Cantor Lectures). "Elementary Art Education," by J. Liberty Tadd.

Tuesday, 29th.—Society of Arts, 8. "Some Examples of Romanesque Architecture in North Italy," by Hugh Stannus.

Wednesday, 30th.—Society of Arts, 8. "Evolution of Form in English Silver Plate," by Percy T. Macquoid.

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THE CHEMICAL NEWS.

VOL. LXXXIII., No. 2149.

TOTAL ECLIPSE OF THE SUN, JANUARY 22ND, 1898.

OBSERVATIONS AT VIZIADRUG. PART IV. THE PRISMATIC CAMERAS.*

By Sir NORMAN LOCKYER, K.C.B., F.R.S.

THE report gives full particulars concerning the 6-inch and 9-inch prismatic cameras which were used during the eclipse, and the results obtained. Twenty-four of the photographs are reproduced. A table is given indicating the wave-lengths and probable origins of the 856 lines which have been measured between D and λ 3663.

The investigation shows the probable presence of both arc and enhanced lines of calcium, chromium, iron, manganese, nickel, strontium, titanium, and possibly cobalt, copper, indium, lead, molybdenum, potassium, and rubidium; arc lines of aluminium, barium, carbon, magnesium, sodium, scandium, and possibly cerium, lanthanum, lithium, rhodium, and tantalum; enhanced lines of vanadium, and possibly of bismuth, cæsium, gold, ruthenium, selenium, silicium, thallium, tin, tungsten, yttrium, zinc, and zirconium. Hydrogen, helium, and asterium are also present.

No evidence has been found of the presence of antimony, arsenic, cadmium, iridium, mercury, osmium, palladium, platinum, silver, or thorium. Further investigations of the coronal rings have led to no definite results regarding their origins.

THE THERMO-CHEMISTRY OF THE ALLOYS OF COPPER AND ZINC.*

By T. J. BAKER, B.Sc., King Edward's School, Birmingham.

THE heats of formation of a number of alloys of copper and zinc, containing those metals in very diverse proportions, have been ascertained.

The method consists in finding the difference between the heats of dissolution, in suitable solvents, of an alloy, and of an equal weight of a mere mixture containing the metals in the same proportion.

The first series of experiments was made with an aqueous solution of chlorine as solvent. Its application was limited to those alloys containing less than 40 per cent of copper, as it was impossible to obtain those richer in copper in a sufficiently fine state of division to enable them to dissolve.

The results, though not altogether satisfactory, showed that the heat of dissolution of an alloy was sensibly less than that of the merely mixed metals.

Incidentally it was found that the equation $Cl_2.Aq = 2600$ (Thomsen's "Thermochemische Untersuchungen"), is erroneous, and on inquiry, Professor Thomsen gave a corrected value, 4870. The author finds $Cl_2.Aq = 4970$.

The most suitable solvents of the alloys are—

(*a*). Mixture of ammonium chloride and ferric chloride solutions.

(*b*). Mixture of ammonium chloride and cupric chloride solutions.

The chemical actions involved are simple reductions, and no gases are evolved.

Two series of experiments made on twenty-one alloys yielded very concordant results. They show that heat is evolved in the formation of every alloy of copper and zinc yet tested.

A sharply defined maximum heat of formation is found in the alloy containing 32 per cent of copper, *i.e.*, corresponding to the formula $CuZn_2$. It amounts to 52·5 calories per grm. of alloy, or 10,143 calories per grm.-molecule. There is some evidence of a sub-maximum in the alloy nearly corresponding to CuZn.

From these points there is a steady decrease in the heat of formation, both in the case of alloys containing less than 32 per cent of copper as the amount of copper decreases, and also in the case of those containing more than 50 per cent of copper as the quantity of copper increases.

The results, in general, confirm the existence of intermetallic compounds, and the values obtained are in accordance with those demanded by Lord Kelvin's calculation of the molecular dimensions of copper and zinc.

THE PREPARATION OF ZINC ETHYL.*

By ARTHUR LACHMAN.

ABOUT three years ago I published a brief outline of a method of preparing zinc ethyl (*Am. Chem. Journ.*, 1897, xix., 410). As is well known, the chief difficulty in this preparation is to secure a suitable form of zinc; and this difficulty was overcome by the use of zinc dust, which is both cheap and plentiful. My note, though brief, contained all the information needed for the immediate application of the process; and a more detailed description would be entirely unnecessary, were it not that a zinc-dust method (Simonowitsch, *Chem. Centrbl.*, 1899, i., 1066) has since then been published which does not appear to offer any advantages over the older one. The two methods differ in that Simonowitsch uses zinc-dust mixed with filings, whereas my process is to be regarded as a modification of the Gladstone-Tribe method (*Journ. Chem. Soc.*, xxxv., 569) in that it uses an alloy of zinc-dust with copper. The method of Gladstone and Tribe has long been recognised as yielding by far the best results; and the only obstacle to its universal employment would seem to be the great difficulty of preparing their "zinc-copper couple" in large quantities. Part of this difficulty lies in the fact that they use zinc filings for this purpose—for filings are hard to procure in quantity; the chief obstacle, however, is that great manual dexterity is required for the successful alloying of the two metals. Moreover, a number of operations are called for; the filings must be freed from oil, they must be cleaned with acid if appreciably oxidised, and then carefully dried; the copper must be prepared by careful reduction of its oxide, and finally the two metals must be alloyed with such care that only small amounts can be taken at one time. As my method yields unlimited quantities of alloy in a single operation, which is automatic and does not occupy more than twenty minutes' time, and as it furnishes an excellent yield of zinc ethyl, it may fairly claim to be an improvement upon its progenitor. The details of the new method proposed by Simonowitsch will be considered by the side of the corresponding details of my own.

1. *The Zinc Dust-copper Couple.*

Gladstone and Tribe have shown that the best yields are obtained when zinc and copper are alloyed in the proportions of about 9 to 1. Zinc dust contains an average of 90 per cent of metal, so that the above proportions are approximated if 100 parts of zinc dust are mixed with 12 parts of copper oxide, and then reduced by heating in a current of hydrogen.

* Abstract of a Paper read before the Royal Society, January 17, 1901.

* Contributions from the Chemical Laboratory of the University of Oregon. From the *American Chemical Journal*, XXIV., No. 1

100 parts zinc dust and 12 parts copper oxide (in the finest possible powder*) are thoroughly mixed and placed in a long glass tube. This tube, which may be of soft glass, should be as wide as the channel of a combustion furnace will permit; at distances corresponding to the length of the channel it should be narrowed to about half its diameter. A plug of glass-wool is fitted into one constriction, the tube then filled about one-half full, and a plug inserted into the other end. The tube is now shaken and rotated in a horizontal position until the mixture spreads out in an even layer. A moderate current of dry hydrogen is then passed through the tube, and the latter heated in the furnace. It is not a difficult matter to properly regulate the heating, a flame of about 5 to 10 c.m. being needed according to the construction of the furnace. The only essentials are to heat the whole tube at once, to rotate the tube one-quarter turn at an interval of a few minutes, and not to be afraid of heating too strongly. It has succeeded best when the powder has slightly baked together, and must be dislodged by a stout wire. Reduction is complete within twenty minutes from the start. The alloy looks much lighter than the mixture, and is considerably coarser, though still a fine powder, The contents are allowed to cool in hydrogen (best by removing the tube from the furnace), and are shaken out when no longer hot to the touch. It is advisable to use as soon as possible, though I have kept the alloy several days in an ordinary glass-stoppered bottle without noticeable deterioration.

It will be seen that this method is much more expeditious than the one given by Simonowitsch. The latter first cleans the zinc dust with dilute acid, washes, and finally dries it in a current of carbon dioxide at a definite temperature. This prepared dust must then be mixed with a considerable proportion of dry, clean filings. It has already been pointed out that filings are hard to obtain.

2. *First Stage of the Zinc Ethyl Synthesis.*

The action of zinc upon ethyl iodide, as is well known, proceeds in two entirely distinct phases. The first consists in a direct addition of ethyl iodide to zinc:—

$$Zn + C_2H_5I = Zn\begin{matrix} I \\ C_2H_5. \end{matrix}$$

It is carried out at the temperature of the water-bath, and its completion becomes manifest by the disappearance of the ethyl iodide. It is customary to carry out this reaction with a great number of complications, such as a mercury valve for increasing the pressure as well as the boiling-point of the liquid (Simonowitsch uses this device), a current of dry hydrogen for keeping out the air, &c. But these are all unnecessary. Equal parts of alloy and ethyl iodide are simply placed in a flask connected with a long reflux condenser, and the mixture kept *gently* boiling on the water-bath until no more ethyl iodide drops back. Violent boiling may drive some of the liquid through the condenser. The time varies from thirty to sixty minutes, according to circumstances that cannot be rigorously defined. I have found it preferable to work with small quantities at a time (from 150 to 250 grms. each of alloy and iodide), to use an Erlenmeyer flask of about 500 c.c. capacity, and to take pains to spread the alloy in a thin, even layer on the bottom. The speed of reaction seems to depend on the surface of metal exposed;† and this would appear to be the reason why Simonowitsch introduces zinc filings into his flasks.

It is a curious fact that the longer the time required for completing this reaction, the more does a secondary process take place resulting in the formation of butane and consequent loss of zinc ethiodide:—

$$2C_2H_5I + Zn = (C_2H_5)_2 + ZnI_2.$$

This is an additional reason for desiring rapid action. Once the ethyl iodide is all used up, the process can be indefinitely interrupted at this point, if not convenient to proceed to the final stage.

3. *Second Stage of the Synthesis.*

The conversion of zinc ethiodide into zinc ethyl according to the equation $2C_2H_5ZnI = Zn(C_2H_5)_2 + ZnI_2$, is accomplished by heating to 180—220°. The flask containing zinc ethiodide is fitted with a double-bored cork, through which connection is made with a condenser and with a generator furnishing dry carbon dioxide. The current of gas should be moderately rapid at first, very slow during distillation, and rapid again at the end in order to wash out the remaining few cubic centimetres in the flask. The zinc ethyl should be purified by re-distillation, as it invariably contains a small amount of unchanged ethyl iodide; for this reason a distilling flask of suitable size should serve as a receiver, to avoid subsequent transfer. The heating is best accomplished in an oil-bath. In my former note I recommended the use of asbestos air-baths as being cleaner and more expeditious; but this advantage is more than offset by the occasional bursting of a flask at the height of the distillation. Fifteen or twenty minutes suffice for this operation.*

The re-distillation of zinc ethyl may be conducted with little trouble as follows:—The distilling flask is carefully connected with a condenser; the receiver, which should be a stout Erlenmeyer flask, is filled with carbon dioxide, and fitted to the condenser with a cork from which a good sized wedge has been removed. A current of carbon dioxide is now delivered almost at the surface of the liquid, and continued until all of the air has been expelled from the apparatus. It is desirable to fit the tube into the flask with a cork, and make the gas escape at the receiver. The gas-jet is now replaced with a thermometer already fitted to a cork, and the distillation carried out as with ordinary liquids; a free flame may be used with perfect safety. All flasks to be used as receivers must be filled with carbon dioxide, and fitted with good sound corks. To change receivers, fasten the carbon dioxide jet used above so as to play a strong current upon the mouth of the first receiver; gently disengage this from the wedge-shaped cork, and then quickly change flasks, *devoting attention primarily to the new receiver*; the old one may be left with impunity for several minutes, if necessary, before being corked.

4. *The Preparation of Zinc Ethyl in Quantity.*

The process just outlined applies to a single flask of, say, 200 grms. charge, which will yield on an average 60 to 70 grms. zinc ethyl. The time required for all operations except re-distillation is at most one and one-half to two hours, usually not much more than one hour. The method is peculiarly advantageous, however, when it is desired to prepare several hundred grms. at one time. I have already mentioned that the yields are better if not more than 250 grms. be employed in a single operation; but by judicious planning it is not difficult to prepare practically unlimited quantities in a single working day. For this purpose select from three to six flasks of the same aperture, so that all fittings shall be interchangeable. Begin operation by preparing a tubeful of alloy (my tube will hold about 350 grms.). While this is heating, mount two condensers in connection with water-baths, and prepare the corks. As soon as the alloy is ready, charge two flasks and prepare more alloy. As these processes require almost no attention, employ the interval to fit up the condenser, oil-bath, and fittings for the second heating. As soon as a flask is ready, wipe it dry, and heat in the oil-bath (which may be warmed to about 110° or even more); then place a third charge upon the water-bath, &c. By

* This is a commercial article.

† During the boiling little or no liquid penetrates through a thick layer of the powder.

* The *total* time required is one and one-half hours. Simonowitsch needs two to two and one-half hours, not including the time needed for preparing the metal.

these alternations little or no time is lost, and, employing three condensers as described, about 75 grms. per hour will be obtained for each hour after the first (*i.e.*, 75 grms. in two hours, 150 grms. in three hours, &c.). Of course, any greater number of baths and condensers may be employed, if room and assistance permit. I have always worked alone, and have had plenty of spare time working as above.

5. *The Manipulation of Zinc Ethyl.*

The peculiar property possessed by zinc ethyl of rapidly heating itself to the kindling point in air, naturally renders caution necessary when making use of it. In the last few years I have had occasion to handle several kilos. of the substance, and have avoided all mishaps by very simple precautions. On the other hand, the very elaborate appliances which have been devised and recommended for this purpose are very likely to deter many from employing this classic synthetic reagent. I may therefore be permitted to summarise my experiences in this direction.

In the first place, all vessels which are to contain zinc ethyl must be filled with dry carbon dioxide. For drying purposes I use a long tube filled with calcium chloride, and two Muencke wash-bottles containing sulphuric acid. The vessels must be kept corked until used. Secondly, as has been demonstrated by Frankland, caoutchouc stoppers and connections must be avoided, and nothing but dry, sound corks exposed to the vapour of zinc ethyl. Thirdly, the transfer of zinc ethyl is greatly facilitated by pouring it from Erlenmeyer flasks which have perfectly straight sides; and these flasks must be strong enough to withstand sudden and energetic corking. It is inexpedient to attempt the isolation of definite quantities of the reagent; it is much better to pour out the amount needed approximately, and to suit the amounts of other substances to this. The amount taken is given by the loss in weight of the stock vessel; this is not a very accurate procedure, but answers all practical purposes. Fourthly, zinc ethyl may be poured from one vessel to another with perfect safety if the operation is carried out under an inverted funnel of from 4 to 6 inches in diameter, through the stem of which a rapid current of carbon dioxide is passing. After pouring, the first care belongs to the storage vessel; the other readily takes care of itself for some time. This simple expedient does away altogether with the "assistant" (Meyer-Jacobson, "Organic Chemistry," vol. i., p. 284), usually deemed indispensable when handling zinc ethyl. Finally, everything likely to be needed should be ready in advance, so that no time need be lost. It not infrequently happens that the carbon dioxide generator gives out at a critical moment. I make it an invariable practice to have two on hand, so that the second one may be coupled up without delay.

The chief inconvenience in the preparation of zinc ethyl is the cleaning of apparatus after it is all over. It therefore pays to make up as much as possible at one time. If not needed at once, I keep it in flasks of about 200 c.c. capacity, which are about half filled; these are tightly corked, and kept for safety in a large, lead-lined box with metal cover. The substance has been stored this way for months at a time, with no trouble and with practically no loss by oxidation.

6. *Experimental Results.*

The following tables will give the data for all the preparations of which I have kept a record; they are not selected, but include the poorest as well as the best I can find in my note-book.

Velocity of First Stage.

Amount of each reagent taken, in grms.	Time in minutes for disappearance of ethyl iodide.
150	50
150	48
200	45
300	65
75	30

Complete Data.

Iodide used in grms.	No. of separate charges.	Time for completion in hours.	Yield.	Theory.
650	7	4	216	256
300	2	2	95	108
1300	13	10	420	512
500	3	2·5	165	195

These experimental results bear out the claim that the method is quick, certain, and efficient. They correspond to a total yield of 84 per cent in the preparation of nearly 1 kilogrm. It should be remarked that in no case was an attempt made to hurry, and that usually I was at the same time busy with other work.

7. *The Recovery of Iodine.*

The recovery of the iodine which serves as a carrier of energy in this preparation is an exceedingly important affair from the standpoint of laboratory finance. The following method is the one I have found best after many trials:—

After heating in the oil-bath, the contents of the flasks form a solid cake. This is broken up with a sharp stick while still warm (it should be remembered that the contents are more valuable than the flask), and dropped into a bucket of water. After standing over night, the liquid is decanted, and the residue washed with water three or four times. A large bulk of liquid is an advantage. The solution is well mixed, and the amount of iodine determined either by analysis or by computation if the quantity of original ethyl iodide is known. After distributing the liquid among several large flasks, which should not be more than half full, add to each the calculated amount of potassium chlorate necessary to free all the iodine, and an excess of commercial hydrochloric acid. After an hour or more all the iodine will have settled; if the liquid should grow very warm, which happens when it is too concentrated, cool by standing in water. Decant the acid fluid, wash twice with water, and filter the iodine on a Buchner "nutsche." Press the pulp down hard with a pestle, and draw air through it for several hours.

The iodine thus prepared is by no means dry, but it can be easily used for making ethyl iodide. For this purpose, use as many c.c. of ordinary alcohol as there are grms. moist iodine, and take 1/20 the weight of the latter of red phosphorus.] From 2000 grms. iodine I obtained 1720 grms. distilled ethyl iodide in this manner. Thus it becomes possible to make a limited quantity of iodine furnish a practically unlimited amount of zinc ethyl.

THE TITRATION OF SALICYLIC ACID, SALICYLATES, AND PHENOL.

By FERNAND TELLE.

WHEN we add an excess of bromine to a solution of salicylic acid, or of a neutral salicylate, we obtain a precipitate of di-bromosalicylic acid. We have made quite certain that no matter what quantity of bromine may be used in proportion to the salicylic acid present, this is the only bromised derivative formed under the existing conditions:—

$$C_6H_4{<}^{CO_2H}_{OH} + Br = C_6H_2Br_2{<}^{CO_2H}_{OH} + 2HBr.$$

We see that one molecule of salicylic acid (138) requires four atoms of bromine (320). The amount of bromine absorbed by a salicylate is thus proportional to its richness in salicylic acid, and it is on the measurement of the quantity of bromine absorbed that the process we are about to describe rests.

Two methods are at present employed for measuring the amount of bromine absorbed by certain bodies under analogous conditions:—

1. To a solution of the material under examination, titrated bromine water is added until the slightest excess of the reagent is detected by an indicator, such as indigo, for example; this is the method adopted by M. François for the titration of aniline. In this manner the necessary volume of the reagent is determined directly.

2. A known quantity of bromine is added in such a manner that this metalloid will be in excess; the free bromine is then estimated by causing it to act on iodide of potassium, and then measuring the quantity of iodine displaced by a titrated solution of hyposulphite of soda. By difference we get the quantity of bromine that has been fixed. MM. Schlagdenhauffen and Braun determined the amount of bromine absorbed by fatty bodies in this manner.

We have endeavoured to avoid the use of titrated bromine water; this reagent, which is very disagreeable to use, so easily loses its strength, that, according to M. François, it ought to be standardised each time the burette is filled.

Since the application of the second process to the case in which we are concerned, we have observed another disadvantage; starch emulsion is used as an indicator at the end of the reaction, now the flocculent precipitate of dibromosalicylic acid retains the iodide of starch with such persistence that the blue colour which it takes does not disappear on the addition of hyposulphite.

It is for these reasons that, in order to produce the reaction, we prefer to use nascent bromine, given off by the action of a titrated solution of hypochlorite of sodium on a solution of bromide of potassium acidulated with hydrochloric acid.

The titrated solution of hypochlorite is prepared in such a manner as to give about 3·55 grms. of disposable chlorine per litre (a quantity corresponding with 8 grms. of bromine and 3·45 grms. of salicylic acid). This is obtained by diluting about 35 c.c. of commercial hypochlorite to 30 chlorometric degrees with distilled water so as to make one litre of solution.

The strength of this solution is maintained for at least a month if we take the precaution of keeping it away from the light. It is titrated by Gay-Lussac's method with the same author's chlorometric solution, or with a solution containing 4·95 grms. of arsenious anhydride per litre, a quantity corresponding to exactly 8 grms. of bromine, or to 3·45 grms. of salicylic acid. We use bromide of potassium as an indicator at the end of the reaction, as already recommended by M. Denigès; the yellow colouration communicated to the liquid by a slight excess of bromine, suffices to show the end of the reaction in the clear solution; but if the liquor contains a precipitate in suspension, we prefer to shake for some time with a few c.c. of chloroform, which concentrates the bromine set at liberty into a small volume.

We operate on 20 c.c. of arsenical solution, to which we add 5 c.c. of a solution of KBr at 10 per cent. We pour into this mixture, by means of a graduated burette, the hypochlorite solution, stopping when the last two drops added cause the appearance of a persistent faint yellow colour.

Let x be the number of cubic centimetres used; from this we deduce that 1 c.c. of this solution corresponds to $\frac{0{\cdot}0634}{x}$ grm. of Cl, $\frac{0{\cdot}1428}{x}$ grm. of Br, or $\frac{0{\cdot}0616}{x}$ grm. of salicyclic acid, if we have used Gay-Lussac's solution; if, on the other hand, we have made use of the arsenical solution described above, we get $\frac{0{\cdot}071}{x}$ grm. of Cl, $\frac{0{\cdot}160}{x}$ grm. of Br, or $\frac{0{\cdot}069}{x}$ grm. of salicylic acid.

Titration of Salicylic Acid.—1 grm. of the acid to be tested is dissolved in a mixture of 2 c.c. of soda-lye, and about 50 c.c. of water; when dissolved, the volume is made up to 500 c.c. with distilled water. About 25 c.c. of this solution (that is, 0·050 grm. of the substance) are taken, 5 c.c. of 10 per cent. KBr are added, and 10 to 15 drops of hydrochloric acid (too great an excess of HCl delays the absorption of the bromine). The graduated burette being filled with the titrated solution of hypochlorite; this latter is run, drop by drop, into the solution of salicylate with continuous stirring; the bromine is gradually absorbed as it is evolved, and soon a precipitate of bromosalicylic acid is formed. The addition of hypochlorite is continued until the mixture, after agitation, shows faint but evident yellow colouration, which is more apparent after the deposition of the precipitate; to prevent any error, we prefer to add 5 c.c. of chloroform, and the same quantity of alcohol, to prevent the formation of an emulsion, and then to shake vigorously. The precipitate dissolves in the chloroform; this latter is allowed to collect, which is accelerated by the addition of the alcohol, and the end of the operation is indicated by the yellowish tint which the solvent takes by reason of the presence of a trace of free bromine.

The operation can be easily carried out in an Erlenmeyer flask of 375 c.c. capacity; the separation of the chloroform is effected by inclining the flask at an angle of 45°, and giving it a rapid gyratory movement.

Knowing the strength of the hypochlorite solution, we can easily ascertain the richness of the substance under examination, from the number of c.c. used. In spite of the small amount of material operated upon, the estimation is exact because of the relatively large amount of bromine required by such a quantity of material.

A sample of commercial amorphous salicylic acid absorbs 2·305 grms. of bromine (theoretical quantity, 2·318 grms.) per grm., which corresponds to a richness of 99·47 per cent.

Salicylates of Soda, Lithia, and Magnesia.—We proceed as with salicylic acid; 1 grm. of the substance is dissolved in 500 c.c. of water (it appears to be unnecessary to use soda), and 25 c.c. of the solution are titrated as has been explained in the case of salicylic acid.

A sample of salicylate of soda has given the following result:—

Salicylic acid, per cent . .. 85·30 (theoretically, 86·25).

This quantity corresponds with 98·9 per cent of pure salicylate of soda.

A sample of salicylate of lithia gave—

Salicylic acid, per cent . .. 95·05 (theoretically, 95·83).

Which represents a richness of 99·18 per cent.

Two samples of salicylate of magnesia gave—

	I.	II.
Salicylic acid (per cent) ..	78·34	78·0
Magnesia (per cent)	11·2	11·3

by calcination and transformation of the residue into sulphate. At the same time we obtain by calculation—

	For $(C_7H_5O_3)_2Mg,H_2O$. Per cent.	For $(C_7H_5O_3)_2Mg,3H_2O$. Per cent.
Salicylic acid ..	87·34	78·40
Magnesia	12·65	11·36

We see that the quantity of salicylic acid obtained corresponds very closely with that of the magnesia, and that the commercial salt answers to the formula $(C_7H_5O_3)_2Mg,3H_2O$.

Salicylate of Bismuth.—1 grm. of salicylate of bismuth is rubbed up with 25 to 30 c.c. of water, 3 c.c. of soda-lye at 30° are added, and the whole boiled for ten minutes. After cooling, the volume is made up to 250 c.c., and the whole filtered; on 20 c.c. of the filtered solution (corresponding to 0·10 grm. of salicylate), the salicylic acid is estimated by means of the titrated solution of hypochlorite according to the method already described.

The following are the results obtained from two samples:—

	I.	II.	Calculated for $C_6H_4<^{CO_2Bi(OH)_2}_{OH}$
	Per cent.	Per cent.	Per cent.
Salicylic acid	31·79	33·88	36·22
Oxide of bismuth, Bi_2O_3	58·60	60·20	61·41

It is specially in the estimation of this salicylate that our method will be found applicable; the commercial salts are of very variable composition, and the estimation of salicylic acid by the gravimetric method takes rather a long time.

The "codex" shows that officially the salt should contain 61 per cent of the oxide, which can be very easily verified by calcining 1 grm. of the product with nitrate of ammonia, and weighing the residual oxide of bismuth, but this test does not throw much light on the composition of a product which, by the simple action of the water used to wash it, loses salicylic acid, and thus becomes richer in oxide of bismuth. It may also contain other salts of bismuth.

It should be further remarked that the two samples we have analysed contain a larger proportion of oxide of bismuth than that corresponding to the salicylic acid found.

To finish our remarks about salicylic acid and the salicylates, we may say that benzoic acid does not absorb bromine under the conditions described; this enables us to separate the two acids very easily.

On the other hand, for the determination of the purity of commercial salicylic acid there only exist, as far as we are aware, qualitative methods based on the colouration of the crystals resulting from the evaporation of the alcoholic solution of an impure material, or on the fact it communicates to its solution in concentrated sulphuric acid.

The Titration of Phenol.—A dilute solution of phenol, treated with bromine, under the same conditions as those described in the case of salicylic acid, also gives only one derivative, the tribromophenol—

$$\underset{94}{C_6H_5.OH} + \underset{6\times80=480}{6Br} = C_6H_2Br_3.OH + 3HBr.$$

From this it results that the same method of estimation can be applied to phenol. The titration of the hypochlorite solution can be made in the same manner, and x being the number of c.c. of this solution used in operating on 20 c.c. of arsenical solution, we know that 1 c.c. corresponds to $\frac{0{\cdot}0279}{x}$ grm. of phenol if we have used Gay-Lussac's solution, or to $\frac{0{\cdot}0313}{x}$ grm. of phenol if we have used the arsenical solution of which 1 litre corresponds to 8 grms. of bromine.

To make the estimation of a sample of phenol, we dissolve 1 grm. in a litre of water. We measure off 25 c.c. of this solution, and add 5 c.c. of 10 per cent KBr, and 10 drops of hydrochloric acid. By means of a graduated burette we run in the hypochlorite solution; the method of working is, as can be seen, identical with that used for the titration of salicylic acid, and the end of the operation is shown in the same manner by the yellow colouration that the excess of bromine gives to the solution; but it is not necessary in this case to shake up with chloroform, as the precipitate of tribromophenol formed becomes agglomerated on shaking, which enables us to observe the colour of the limpid solution between the flocks of precipitate. Knowing the strength of the hypochlorite solution we can easily calculate the richness of the material analysed. In this manner we obtained, with two samples examined, 99·07 and 99·65 per cent of pure phenol.

The titration of a phenic solution at 1/1000th can be similarly carried out on 25 c.c. of this solution, and that of a phenic solution at 1/100th on an equal volume of the same solution previously diluted with ten times its volume of water.

Salicylate of Phenol.—The method of estimation we have just described, which can be used both for salicylic acid and for phenol, necessarily applies also in the case of salol, if we do the titration on the product of saponification of this body. One molecule of salol then uses 10 atoms of bromine (of which 6 are for the phenol and 4 for the salicylic acid).

The titration of the hypochlorite solution being always effected in the same manner, we find that 1 c.c. of this solution is equivalent to $\frac{0{\cdot}0382}{x}$ grm. of salol if the titration is done with Gay-Lussac's solution, and to $\frac{0{\cdot}0428}{x}$ grm. if we use the arsenical solution corresponding to 8 grms. of bromine per litre.

The following is the method used for titrating a sample of salol:—We weigh out 0·25 grm. of salol, and place it in a 100 c.c. flask; we add 2 c.c. of soda-lye at 30° B. and about 20 c.c. of water, then boil for a few minutes. After cooling, the volume is made up to 100 c.c.; we shake well, and then take 10 c.c. of the solution, on which the titration with hypochlorite is done after the addition of 5 c.c. of KBr at $\frac{1}{10}$th, and 15 drops of hydrochloric acid, following the same manner of working as has been described for the estimation of phenol.—*Journ. de Pharm. et de Chim.*, Series 6, vol. xiii., No. 2.

A BIBLIOGRAPHY OF STEEL WORKS ANALYSIS.

PART VII.

By HARRY BREARLEY.

(Continued from p. 40).

CHROMIUM (*continued*).

III. VOLUMETRIC ESTIMATION OF CHROMIUM.

III.*a. With Ferrous Salts.*—

996. BRITTON (*C. N.*, xxi., 266).—Ignite ore with $KClO_3$ and soda-lime, dissolve in dilute HCl, and titrate with $FeSO_4$ and $KMnO_4$.

997. CLARK (*C. N.*, xxiv., 286). — Ignite ore with $NaHO + MgO$, and titrate sulphuric solution with $FeSO_4$ and $K_2Cr_2O_7$.

998. CLARK (*J. S. C. I.*, 1893, 340).—Dissolve steel in HCl, precipitate Cr with Na_3PO_4 and Na_2SO_3, oxidise ignited precipitate with MgO and NaHO. Chromic oxide may also be precipitated as basic sulphite and, if pure, ignited to Cr_2O_3.

999. SCHWARZ (*C. N.*, xlix., 201).—The CrO_3 formed by alkaline fusion is added to excess $FeSO_4$, and titrated with $KMnO_4$. Pouring $FeSO_4$ into K_2CrO_4 may cause error through formation of chromic chromate.

1000. MCKENNA ("Methods of Iron Analysis," p. 121, Pittsburg).—Dissolve in HCl, replace HCl with HNO_3, add $KClO_3$, boil to decompose it, and titrate CrO_3 with permanganate. Powalleck (*C. N.*, li., 83) also oxidises and titrates in this way.

1001. GALBRAITH (*C. N.*, xxxv., 151).—Dissolve steel in dilute H_2SO_4, oxidise with $KMnO_4$, and titrate filtered solution with $FeSO_4$, &c.

1002. PETERSON (*C. N.*, l., 210).—As 1001; add $KMnO_4$ to the H_2SO_4 solution until MnO_2 is plentifully formed.

1003. VIGNAL (*C. N.*, liii., 195).—A good account of the process depending on oxidation with permanganate. Dissolve iron by preference in HNO_3. The formation of MnO_2 roughly indicates the amount of Cr present.

1004. Arnold (*C. N.*, lxxi., 292).—In strong H_2SO_4 solutions, oxidation to CrO_3 with permanganate is impossible.

1005. Galbraith (*J. I. S. I.*, 1893, i., 146).—Presence of Fe favours accuracy of process 1001. Modifies process by adding NaHO, filtering off MnO_2, $Fe_2(HO)_6$, &c., and titrating the filtrate.

1006. Barba (*J. I. S. I.*, 1893, ii., 536).—Condemns process 1005. Dissolve in HNO_3, oxidise, precipitate Mn, Fe, &c., with AmHO, but re-dissolve the Fe in H_2SO_4, and titrate the filtrate.

1007. Brearley (*C. N.*, lxxvii., 131, 187, and 216).—Manganous salts precipitated with NaHO in presence of CrO_3 partly reduce it. Process 1005 subject to error on this account.

1008. Wahlberg (*J. I. S. I.*, 1889, i., 398).—Dissolve in HNO_3, ignite dried residue with Na_2CO_3, $KClO_3$, and MgO, and titrate the filtered CrO_3.

1009. Dittmar ("Quant. Chem. Anal.," p. 128).—Fuse chromite with borax-glass + $NaKCO_3$, and titrate the acid extract. Instructions for complete analysis of ore.

1010. Stead (*J. I. S. I.*, 1893, i., 153).—Examination of 1001. Avoid filtration of MnO_2 by dissolving in HCl and boiling off Cl. Or precipitate from ferrous solution as phosphate, ignite with $NaKCO_3$ + MgO, and titrate CrO_3. $BaCO_3$ does not precipitate Cr_2O_3 completely from ferrous solutions. Precautions against V. Chromeisen also oxidised by the above (tribasic) reagent, and extract titrated. Distribution of Cr in British irons.

1011. Leffler (*C. N.*, lxxvii., 156).—MnO_2 is soluble in strong H_2SO_4. Such a solution can oxidise $FeSO_4$, and may lead to error in processes like 1001.

1012. J. T. (*C. N.*, lxxix., 158).—When chromeisen is oxidised in the dry way and the frit dissolved in acid, some very fine portions of the alloy, having escaped oxidation, will exert a reducing action on the CrO_3.

1013. Schneider (*J. I. S. I.*, 1892, ii., 515).—Oxidise nitro-sulphuric solution of the steel with PbO_2; decompose any permanganate formed by making alkaline and boiling. Titrate with $FeSO_4$.

1014. Harvey (*C. N.*, xlvii., 86).—Heat CrO_3 compound with HCl + $SnCl_2$, add Fe_2Cl_6, and determine FeO with $K_2Cr_2O_7$.

1015. Schneider (*J. I. S. I.*, 1886, 399). — Dissolve chromeisen in H_2SO_4, oxidise solution of dried residue with Br, precipitate Fe with AmHO, and titrate the filtrate.

1016. Spüller and Kalmann (*J. I. S. I.*, 1893, ii., 537). —Fuse chromeisen with soda peroxide, decompose excess by passing CO_2, and titrate the acidulated filtrate.

1017. Spüller and Brenner (*J. I. S. I.*, 1897, i., 570).—Modified process for FeCr. Acid solution of steel dried, fuse as FeCr, and CrO_3 estimated iodometrically.

1018. Saniter (*J. I. S. I.*, 1895, ii., 153).—Fuse FeCr with mixture of Na and Ba peroxides, and boil acidified solution with permanganate according to Stead's modification (1010) of 1001.

1019. Rideal and Rosenblum (*J. S. C. I.*, 1895, 1017).—Severe criticism of 1018. Ni from fusion crucible interferes with the ferrocyanide indicator. Mn, Ni, and Fe separated before titration. The uses of Na_2O_2 in chrome-iron and steel analysis.

1020. Saniter (*J. S. C. I.*, 1896, 155).—Discusses the criticisms of 1019.

1021. Carnot and Goutal (*J. C. S.*, lxxii., ii., 521).—Treat with Cu solution (993), fuse residue with Na_2O_2, and titrate CrO_3.

1022. Kosmann (*J. I. S. I.*, 1889, ii., 479).—Oxidise the Fe solution with alkaline H_2O_2, and titrate a filtered fraction with $FeSO_4$.

III.*b. Iodometric Estimation of Chromium.*—

1023. Waller (*J. S. C. I.*, 1896, 436).—Decompose ore with Na_2O_2, and titrate CrO_3 with $Na_2S_2O_3$ and KI.

1024. O'Neill (*C. N.*, v., 199). — Fuse ore with $KHSO_4$, precipitate with Na_2CO_3, fuse with Na_2CO_3 + $KClO_3$, and titrate CrO_3 with $Na_2S_2O_3$, using KI and starch as spot indicator.

1025. Zulkowski (*C. N.*, xix., 238).—Add KI to an HCl solution of CrO_3, and titrate liberated I.

1026. Sell (*C. N.*, xxxix., 131).—Fuse chromite with bisulphate and soda fluoride, oxidise with $KMnO_4$, add Na_2CO_3 and alcohol, and estimate CrO_3 with KI.

1027. Sell (*C. N.*, liv., 299).—Oxidise with H_2O_2 in alkaline solution, and titrate CrO_3. Al and Zn are without influence; Fe (filtered off) causes low results.

1028. Browning (*J. C. S.*, lxxii., ii., 73).—Add excess As_2O_3 and $NaHCO_3$ to CrO_3 solution, and titrate with I. Ferric salts may be present. Also, Namias (*J. C. S.*, lxii., 1374) and Bialobrzeski (*J. C. S.*, lxxiv., ii., 184.—In like manner in the presence of acetates and acetic acid.

1029. Donath (*J. I. S. I.*, 1894, ii., 493).—Pour ferric solution into alkaline permanganate, and estimate the iodine liberated by the CrO_3. $FeSO_4$ not suitable for estimating small amounts of chromic acid.

III.*c. Miscellaneous Volumetric Processes.*—

1030. Davy (*C. N.*, iii., 274) and Rube (*C. N.*, xii., 82).—Titrate acid solution of CrO_3 with ferrocyanide, using Fe_2Cl_6 spot indicator.

1031. Donath (*C. N.*, xliii., 253).—The neutral Cr_2O_3 solution is run into hot alkaline standard $KMnO_4$ until a yellow colour is obtained. Fe and Al do not interfere; Mn does (see 100).

1032. Giorgis (*J. C. S.*, lxiv., ii., 554).—Oxidise alkaline ferric solution with $KMnO_4$, destroy excess with H_2O_2, reduce filtered CrO_3, and run into $KMnO_4$ as in 1031.

1033. Giorgis (*J. C. S.*, lxxii., ii., 350).—Add standard $KMnO_4$ to Cr_2O_3 solution, boil, and titrate excess $KMnO_4$ with N/20 $Cr_2(SO_4)_3$ solution.

1034. Carnot (*J. I. S. I.*, 1889, i., 399) and Perrault (*J. I. S. I.*, 1893, i., 413).—Oxidise to CrO_3 with AmHO + H_2O_2, boil off excess, and titrate with H_2O_2 in acid solution.

1035. Berthelot (*J. C. S.*, lvi., 350 and 468).—The H_2O_2 + CrO_3 reaction varies with the mode of admixture, temperature, and concentration.

1036. Jean and Pellet (*C. N.*, xxxv., 213).—Decompose ore by fusion. To CrO_3 add baryta-water and CO_2 to precipitate excess thereof. The free alkali equivalent to the CrO_3 is titrated with H_2SO_4.

1037. Ruoss (*J. C. S.*, lxxiv., ii., 644).—Add lead salt to CrO_3 solution, and estimate the excess in a fraction of the filtrate.

1038. Soltsein (*J. C. S.*, lx., 118).—CrO_3 titrated with $BaCl_2$, using hæmatoxylin or logwood indicator.

1039. Purgotti (*J. C. S.*, lxxii., ii., 349).—Acidified hydrazine sulphate acts quantitatively with $K_2Cr_2O_7$, liberating N. The N is measured at normal temperature and pressure. Similar process for Cu.

1040. Baumann (*C. N.*, lxvi., 181, &c.).—In acid solutions, H_2O_2 oxidises CrO_3 to perchromic acid and then reduces it to Cr_2O_3. Liberated O gasometrically estimated. CrO_3 formed by H_2O_2 in alkaline liquids. These facts applied extensively to quantitative analysis.

1041. Hillebrand (*C. N.*, lxxviii., 227).—Traces of Cr in rocks, ores, &c., estimated by comparing as mono chromate with standard solutions.

1042. Neumann (*J. C. S.*, lxviii., ii., 64).—By titrating neutral Cr_2O_3 solution with soda sulphide.

(To be continued).

THE DETECTION OF METHYL ALCOHOL IN MIXTURES.*

By S. P. MULLIKEN and HEYWARD SCUDDER.

In a recent article by E. Jandrier (*Ann. Chim. Anal. App.*, iv., 156; *Centrbl.*, 1899, i., 1296, Abstract), it is stated that a test for methyl alcohol described by us in an earlier number of the *American Chemical Journal* (xxi., 266), and based on the oxidation of the alcohol to formic aldehyde, followed by condensation of the latter to a coloured derivative of resorcine, is unreliable, because it is also given by acrolein, and is interfered with by the presence of furfurol. To remedy these defects in our method Jandrier recommends that gallic acid be employed instead of resorcine as the reagent for formic aldehyde, he having found in an earlier investigation (Barbier and Jandrier, *Ann. Chim. Anal. App.*, i. 325; *Analyst*, xxi., 295, Abstract), that the colour reaction obtained by the use of gallic acid is much more delicate and less likely to be obscured by colourations occasioned by the simultaneous presence of other aldehydes.

A careful examination by the authors of this modification of their test soon proved that its use for the purpose proposed is entirely inadmissible, and this despite the fact that gallic acid is actually, as claimed, a better reagent for the detection of formic aldehyde than is resorcine! The explanation of this paradox will be made apparent by a consideration of certain facts that have lately come to our knowledge while studying the partial oxidation by hot copper oxide of a considerable number of organic compounds.

The means chosen for oxidising methyl alcohol to formic aldehyde detailed in our first paper, was the very simple one of plunging a short, closely-wound spiral of light copper wire, previously heated to redness, and superficially oxidised, into the solution to be tested. Special emphasis was placed on the condition that: "A concentrated spirit should always be diluted with at least three or four volumes of water before oxidation." It was also particularly noted that 1 drop of 0·5 per cent resorcine solution was the quantity of reagent that should be added for every 3 c.c. of all solutions originally containing more than 0·1 per cent of methyl alcohol. These minute specifications were necessary, partly because it had been found that absolute ethyl alcohol, when directly oxidised without previous dilution, would, if afterwards largely diluted with water, give a very faint colour reaction resembling that caused by formic aldehyde. This colour was, however, noticed only when the weight of resorcine added to a given volume of solution was many times less than that usually employed, and it first made its appearance after several hours instead of within a few minutes, as usually happened with solutions that really contained methyl alcohol. The conditions necessary for the production of this colour from ethyl alcohol were so unusual, its intensity was so slight, and its course so obscure, that no account of it was included in our first paper. A more suggestive observation was made by us at the same time with reference to the use of caseine, of which we wrote (*loc. cit.*):—"Caseine is not a suitable reagent for methyl alcohol tests, because the oxidation-products of ethyl alcohol yield with it the same blue colour as formic aldehyde; though singularly enough solutions of pure acetaldehyde do not give this result."

After the gallic acid reaction for formic aldehyde had been brought to our attention, we endeavoured to verify the advantages claimed for it in the detection of methyl alcohol. For our purpose it was found best to employ the reagent very nearly in the manner recommended by Istrati.† 0·2 c.c. of a saturated solution of gallic acid in pure ethyl alcohol was mixed with a few drops of the oxidised alcoholic solution to be tested, diluted to 2 c.c., and the mixture carefully run down the side of an inclined test-tube containing a few c.c. of concentrated sulphuric acid. At the line of contact between the two liquids a yellow zone, almost immediately turning green, makes its appearance, if the solution contains formic aldehyde. Above and below the green zone, blue rings then rapidly develope. If other substances which give colour reactions are also present, the upper layer will vary in colour, but the green and the lower blue ring will still appear beneath. The colours are pure and characteristic, and are not obscured by the presence of other aldehydes. Having familiarised ourselves with these phenomena, it was with considerable surprise that we found the oxidation-products obtained in the usual way from the purest procurable ethyl, propyl, isopropyl, secondary butyl, tertiary butyl, and normal butyl alcohols, ethylene glycol, glycerin, acetaldehyde, paraldehyde, ethyl ether, acetone, pinacone, and acetic acid, all gave distinct green and blue rings with gallic acid.

The total failure of the gallic acid test to distinguish the substances enumerated from methyl alcohol, as well as the anomalous results noted in our earlier experiments with the oxidation-products from concentrated ethyl alcohol when tested with a trace of resorcine or with caseine, are susceptible of only two simple explanations. Either all the apparently pure compounds oxidised must have contained methyl alcohol or methyl derivatives as impurities, or the list of compounds which may give traces of formic aldehyde, upon oxidation with copper oxide, is a very much longer one than has hitherto been suspected. The hypothesis that methyl alcohol in small quantities may be formed along with ethyl alcohol in alcoholic fermentations is perhaps not unworthy of a more thorough investigation than it has received. Trillat claims to have detected traces of it in some genuine brandies. But it is, nevertheless, highly improbable that all the cases which have been noted by us in which formic aldehyde reactions were obtained from the oxidation-products of the many presumably pure substances taken for our experiments can be explained in this way, and we inclined strongly, from the first, to the acceptance of the second explanation, the probability of which has since become a certainty in consequence of a supplementary quantitative investigation conducted by one of the authors, with the assistance of Messrs. Brown and French, an account of which will follow later in the *American Chemical Journal*.

The logical justification for adhering to the use of resorcine in the test for methyl alcohol lies, then, in the presumption that no common organic compound that could occur in such solutions as are provided for by the method (with the exception of methyl esters or ethers), will furnish enough formic aldehyde, or other substance, exhibiting a similar behaviour, when treated with due regard to the detailed directions, to give a rose-red ring and flocks. This presumption is a sufficiently well-founded one, when all the precautions that will be given further on in this paper are observed. The gallic acid and caseine tests, on the contrary, must be rejected, because they are so delicate that formic aldehyde may be detected by their use in nearly any organic solution that has been partially oxidised by means of a copper spiral.

Since the publication of our first paper we have had occasion to apply the resorcine test for methyl alcohol to a great variety of mixtures, and as a consequence of the fuller knowledge of the imperfections of the method thus gained, we are now in a position to suggest certain improvements in the original procedure, which, we believe, will considerably augment its practical usefulness. Analysts are, as a rule, too prone to ignore the fact, that the *absolute*

* Contribution from the Chemical Laboratory of the Massachusetts Institute of Technology. From the *American Chemical Journal*, xxiv., No. 5.

† *Analyst*, 1898, xxiii., 230, Abstract, Istrati's original memoir on the colour reactions between aldehydes and phenols (*Buletinul Societatei de Sciinte, Bucuresci*, vii., [2]. 163—170), which was made accessible to us through the kindness of M. Jandrier, forms a continuation of the earlier studies of Barbier and Jandrier. Another still earlier research on the value of phenols for the detection of aldehydes, mention of which was also unintentionally omitted in our first paper, is by Nickel (*Fres. Zeit.*, 1889, 249).

identification of any compound by the use of some single specific reaction is an unattainable end when really unknown mixtures are dealt with. Specific qualitative tests are of great value when judiciously employed; but each new mixture must be considered by itself, and whenever there is reason to suspect the presence of substances which may interfere with the test selected, means for their removal must first be devised. The list of compounds whose presence may mask the colour reactions given by phenols with formic aldehyde is a long one, and includes bodies which are likely to be met with in such important mixtures as the commercial tinctures, extracts, varnishes, alcoholic beverages, and solvents. While it would be feasible to formulate quite definite rules of procedure for the detection of methyl alcohol in any limited group of mixtures, it will be more profitable here to make certain general suggestions that will be of service in the solution of a variety of special problems.

The following precautions should always be observed:

(*a*). Use for the test only that part of any mixture that can be completely distilled at a temperature between 50° and 100°, and which, after distillation, gives a clear colourless solution when shaken with two or three volumes of water.

(*b*). Make a blank experiment, before oxidation with the copper spiral, by pouring 2 c.c. of a clear aqueous solution of the distillate of proper boiling-point, to which 1 drop of 0·5 per cent resorcine solution has been added, so as to form a layer upon concentrated sulphuric acid in a test-tube. If a precipitate or a coloured ring make its appearance, the solution requires further preliminary treatment.

(*c*). Do not test without preliminary treatment any solution that is known or suspected to contain phenols, alkaloids, or organic bases.

The reasons for these precautions are obvious. Many organic compounds give colourations with sulphuric acid alone; others, including nearly all aldehydes and many bases, condense easily with resorcine under the conditions of the test to insoluble or intensely coloured products. Other phenols besides resorcine, and many bases, will, if present, react with any formic aldehyde that may arise by oxidation with the wire, and thus prevent or obscure the appearance of the characteristic rose-red ring.

Methyl alcohol may be separated easily from most colouring-matters, oils, resins, sugars, glycerin, and glycols, by a simple distillation; from phenols and acids by distillation from an aqueous solution containing caustic alkali; from bases by distillation from aqueous solutions strongly acidified with a dilute mineral acid. When small quantities of methyl alcohol are extracted from insoluble organic mixtures by shaking out with water, it is to be remembered that the methyl alcohol will tend to concentrate in the first part of the aqueous distillates obtained from such solutions, and that various aldehydes, phenols, and bases may pass over with it on account of their volatility with steam, and will have to be removed afterwards.

When the preliminary blank experiment (*b*) gives a colouration or precipitate, and the solution gives aldehydic reactions with ammoniacal silver nitrate, and with Schiff's rosaniline-aldehyde reagent, take 12 c.c. of the alcoholic distillate, which, if concentrated, must first have been diluted so as to contain at least 75 per cent of water; place in a small firmly stoppered bottle with 3 grms. of resorcine, and 1 c.c. strong sulphuric acid, and heat for two hours in a water-bath at 70—80°. Cool, dilute the solution to 50 c.c. with water, distil off 5 c.c., and test the distillate for methyl alcohol in the usual manner. Large quantities of aldehydes may be held back by resorcine in this way, though, when the mixture consists mainly of aldehydes, more resorcine and longer heating will be required. An analogous method for accomplishing this same result, which employs aniline and phosphoric acid instead of resorcine and sulphuric acid, was proposed by Allen and Chattaway (*Analyst*, xvi., 102), for use in the analysis of whiskies. We have used both these methods with success upon mixtures containing as high as 50 per cent of furfurol and other aldehydes, thus meeting the chief objection which Jandrier has raised against our procedure.

A more difficult, but practically far more important, problem than that of removing aldehydes from the original mixtures, had to be faced, when we sought to discover some simple means for taking away the acetaldehyde which is always formed together with formic aldehyde when mixtures containing both ethyl and methyl alcohols are oxidised. The most that could be previously claimed for the test with resorcine in such mixtures was that:—"One part of methyl alcohol may be detected without great difficulty in the presence of five parts of ethyl alcohol." A simple and fairly satisfactory way out of this difficulty was, however, found.

Acetaldehyde is easily and completely expelled from aqueous solutions by persistent boiling in a vessel provided with some condensing arrangement that will prevent too rapid loss of water vapour. Dilute solutions of formic aldehyde, on the contrary, lose their aldehyde very slowly under this treatment, it being firmly held, partly in a polymerised condition, by the hot water. Such solutions will, however, lose all their formic aldehyde when the distillation is rapid and is pushed too far. The improved test for methyl alcohol now to be described takes advantage of these facts, and as the procedure not only removes acetaldehyde, but also traces of many other higher boiling substances that exert an injurious influence on the final colour reaction, its employment is generally to be preferred to the somewhat simpler method earlier described by us.

When entirely unknown mixtures are under examination they must, of course, always receive in addition a suitable preliminary treatment, though it has been found that a previous digestion with resorcine and acid for the removal of aldehydes, will seldom be required when these substances are not present in larger quantities than are usually found in the distillates from fermented and distilled liquors.

Unless the mixture to be examined, after receiving what ever preliminary treatment may have been found necessary, already contains much water, dilute 2 c.c. with water until it measures 6 c.c. Treat with the oxidised copper spiral as elsewhere described, six times, cooling the tube with running water after each treatment. Next fit the test-tube, which should have a length of 6—7 inches, with a doubly perforated rubber stopper. One perforation of the stopper is to be fitted with a piece of glass tubing drawn out to a *very fine capillary* whose end is forced down so as nearly to touch the bottom of the tube. Let the wide end of the tube, on which the capillary has been drawn, project an inch above the stopper, and attach to the projecting end a bit of rubber connector which can be closed by a small screw clamp. Fit the second perforation of the stopper with a bit of glass tubing which is placed in connection with a good water-suction pump capable of giving a vacuum of about 20 m.m. Support the test-tube by a clamp, so that it will be two-thirds immersed in water in a beaker maintained at 25—30°. Partially close the screw clamp, and apply gentle suction for a few moments so as thoroughly to saturate the liquid with air. Then screw the clamp tight, and apply suction with the full power of the pump. A rapid stream of gas bubbles, at first principally air, but later consisting of acetaldehyde, alcohol, and water vapour, will rise from the fine capillary point, the liquid boiling under the diminished pressure. Continue this distillation *in vacuo* until just one-half of the liquid has evaporated. This requires about ten minutes. By judiciously regulating the action of the pump, and in some cases admitting a very little air through the capillary, the boiling, though accompanied by some frothing, is easily controlled, and bumping prevented.*

* An experienced operator may often obtain equally satisfactory results by simply boiling down the oxidised aqueous solution in an open test-tube until the moment when the odour of acetaldehyde disappears. The method of boiling down *in vacuo* is, however, in general, much more reliable.

Next add 1 drop of a solution, containing 1 part of resorcine in 200 parts of water to the residual solution, and pour it cautiously into a second tube held in an inclined position in such a way that the two liquids shall not mix. Allow it to stand three minutes; then, holding the tube by its upper end, sway it slowly from side to side in such a manner as to produce a very gentle rotary motion between the two layers. This operation must be persisted in, if necessary, for a minute or more, using a piece of white paper for a background; but must be conducted so gently that only a very gradual and partial mixing of the water and acid shall be caused. Nearly half of the acid should remain as a distinct unmixed layer at the end. When methyl alcohol is present, the shaking causes the separation of more or less voluminous flocks of a very characteristic rose-red colour. The appearance of coloured zones or flocks of other hues, even when tinged with red, or of a rose-red solution without the flocks, should never be considered proof of the presence of methyl alcohol. However, if the flocks are reddish-brown, or if the upper layer has a pronounced red colour, it is often well to repeat the test. Too hasty or careless mixing of the aqueous and acid layers spoils the reaction, which will also fail or give unsatisfactory results if the evaporation *in vacuo* is too long continued, or if it is stopped before the complete removal of all acetaldehyde.

The delicacy of the test as here described is sufficient to permit the detection of 1 part of methyl alcohol in 2000 parts of the solution as prepared for oxidation. If, in a solution of moderate concentration, the proportion of ethyl to methyl alcohol does not exceed 100 parts to 3, entirely satisfactory tests for the latter are obtained without difficulty. When the ratio between the alcohols is 100 : 2, the test is occasionally successful, but cannot be depended upon.

Besides methyl alcohol, the only substances which are known to give the same reaction with the improved resorcine test are the methyl esters and ethers (including methylal), and secondary and butyl alcohols (compounds which are rarely met with except in quantities too small to be readily detected). Acetone and dimethylethyl carbinol give red rings at first, but on shaking, the aqueous layer becomes red-brown without yielding the rose-coloured flocks.

As compared with other qualitative tests for methyl alcohol known at the time of writing, the one just presented is without question the simplest, the most rapid, and the most convenient. Its delicacy, while not great, is sufficient for most practical purposes, and its most serious imperfections are so well defined as to be rendered comparatively harmless.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 17th, 1901.

Professor THORPE, C.B., F.R.S., President, in the Chair.

MESSRS. E. F. Hudson, H. A. Auden, and A. H. Mitchell were formally admitted Fellows of the Society.

The following certificates were read for the first time:—Percival James Burgess, Singapore; Raymond Dubois, Rutherglen, Victoria; Oscar Loewenthal, Mill Hill Park, London, W.; Walter Stevens Crocker, 25, Upper Parliament Street, Liverpool; Herbert Ackerman Tozer, 113, Stepney green, London, E.

The following letter has been sent, at the direction of the Council, to Professor Markownikoff of the University of Moscow, a Foreign Member of the Society, on the occasion of the commemoration of the fortieth year of his Doctorate:—

DEAR SIR,—At the last meeting of the Council of the Chemical Society I had the pleasure of submitting your letter of December 8th, concerning the proposed celebration in honour of Prof. Dr. Wladimir Markownikoff. I am instructed by the Council to inform you that it will not be possible for any of our Fellows to be present personally on February 25th, but I am to ask you to be so good as to convey to Prof. Markownikoff the hearty congratulations of our Society, and to express the wish that he may be spared to carry on his valuable and important investigations for many more years. We rejoice that your distinguished countryman's name appears in our list of Foreign Members, and I beg you to convey to him the assurance that his long devotion to that science which he has done so much to advance by his researches is most highly appreciated by English chemists.

Yours obediently,

RAPHAEL MELDOLA,
Foreign Secretary.

Dr. H. DECKER.

Of the following papers, those marked * were read:—

*1. "*The Preparation of Iodic Acid.*" By A. SCOTT and W. ARBUCKLE.

The usual method of preparing iodic acid by gently boiling iodine with nitric acid in a flask with a long neck, is tedious when any quantity is required, and liable to great loss of iodine unless the source of heat is very carefully regulated. By using, first the ordinary form, and later a modified form, of Soxhlet's fat extraction apparatus to contain the iodine, almost theoretical yields of iodic acid were obtained after a very short treatment with the boiling nitric acid. The liability, however, of the syphon-tube to become choked with crystals of iodic acid led to the abandonment of this type of apparatus. After many trials with various forms of apparatus, the authors recommend the use of a round-bottomed flask having a ground-in neck carrying two tubes, to one of which is sealed a reflux condenser, and through the other is fitted a tube by means of which a current of oxygen is passed through the boiling liquid. With this apparatus *finely powdered* iodine boiled with ten times its weight of fuming nitric acid may be completely oxidised in twenty to thirty minutes.

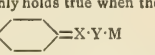
*2. "*Note on Isomeric Change and Meta-substitution in Benzenoid Amines.*" By A. LAPWORTH.

The rules deduced from the two simplest change forms (*Trans.*, 1898, lxxiii., 457) depend on the assumption made implicitly throughout the paper, that only one group can "migrate" along any chain of atoms at any instant; that is, that exchange of groups is, as a rule, the result of the successive migration of the two groups in reverse directions. This view appears in general to be well founded, and it is easily demonstrated that if it holds true, the rules deduced are necessarily correct, the second being used where the valency of an atom alters. It is of no consequence whatever how the migration is effected, so far as the applicability of the rules is concerned.

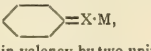
Although in applying the rules it is sometimes convenient to assign successive positions of attachment of a labile group in its migration, it is not imagined that these are actually occupied, at least in the ordinary sense of the term. It may be supposed, for example, that the group is handed on in a still dissociated state from its initial to its final position, the others merely representing the possible places of attachment.

The author has advanced the view that *meta*-substitution is the result of elimination of a hydrogen atom in the benzenoid nucleus (necessarily from the *meta*-position) with a group in the complex formed by union of the side chain with the acting agent. Armstrong has recently used a similar conception in explaining the formation of chloracetanilides from phenylacetylchloramines; in the author's opinion, this would lead to the production of the *meta*-derivative, instead of, as is the case, the *ortho*- and *para*-derivatives (compare *Trans.*, 1900, lxxvii., 1051).

In alluding to the formation of *meta*-sulphonic acids from benzenoid amines (*loc. cit.*, p. 457), the author suggested that it was the result of the migration of the $-SO_3H$ group in aniline sulphates; this view must be rejected as impossible, as the necessary grouping is not present. The statement that *meta*-derivatives are formed when the labile group M is separated from the benzene ring by two atoms only holds true when the grouping—

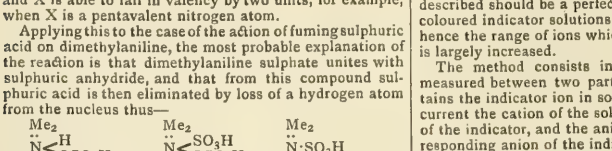


is present or can be formed as an intermediate step. M will migrate to the *meta*-position when separated by one atom only, from the nucleus if the intermediate compound is of the type—



and X is able to fall in valency by two units, for example, when X is a pentavalent nitrogen atom.

Applying this to the case of the action of fuming sulphuric acid on dimethylaniline, the most probable explanation of the reaction is that dimethylaniline sulphate unites with sulphuric anhydride, and that from this compound sulphuric acid is then eliminated by loss of a hydrogen atom from the nucleus thus—



The latter substance must yield the meta-sulphonic acid if the sulpho-group then migrates, assuming, as usual, that the other atoms retain their positions until this migration has ended. Or, expressing it in terms of the author's rules, as the sulpho-group migrates the valency of the nitrogen must fall, since it cannot become attached to the nucleus by a treble binding; the nearest possible position of attachment for the labile group is, therefore the β-position; hence, as the valencies of the carbon atoms remain constant, the next position must be imagined to be reached by an $\alpha\gamma$-change. This process can also be followed by using Thiele's rule, but, in this case, it must be assumed that sulphuric acid is added in one way and eliminated in another, and as for this purpose it must be supposed that before addition it breaks up into HO and $\cdot SO_3H$ instead of into H and OSO_3H, the objection to this hypothesis is obvious,

3. "*The Preparation of Esters from other Esters of the same Acid.*" By T. S. PATTERSON and C. DICKINSON.

Experiments were described which had for their object the preparation of methyl ethyl tartrate. A substance was obtained having the observed rotation $+11\cdot14°$ at 18° (l=200 m.m.), which probably consisted chiefly of the compound sought. It showed no tendency to crystallise, and as no method of purification, other than crystallisation, was likely to be suitable, these attempts to obtain a pure compound were abandoned. They had shown, however, that ethyl tartrate is largely converted into methyl tartrate by the action of methyl alcohol and hydrochloric acid. Experiments were then described showing that pure ethyl tartrate can be obtained from methyl tartrate and pure methyl tartrate from ethyl tartrate, by Fischer's method; hence it is probable that any other ester may be prepared by an analogous process; under certain circumstances this might prove useful.

Finally, determinations of the rotation of methyl tartrate at temperatures between 20° and 100° were given.

4. "*Tecomin: a Colouring-matter derived from 'Bignonia tecoma.'*" By T. H. LEE.

The new colouring-matter is a yellow crystalline substance soluble in alcohol with an orange colour, insoluble or very slightly soluble in water; the solution becomes rose-red with alkalis and clear yellow with acids; 2 c.c. N/100 alkali or acid causes the colour change; it is not affected by any but the strong mineral acids, but the presence of organic acids renders the end-reaction indistinct. The wood contains a reddish brown resin soluble in alcohol, from which it is difficult to free the tecomin; also a deep brown colouring-matter which dissolves in aqueous alkalis and is precipitated by acids. It is used locally as a dye for cotton and as a stain for wood.

5. "*A New Method for the Measurement of Ionic Velocities in Aqueous Solution.*" By B. D. STEELE, B.Sc.

The author described a new method for the direct measurement of ionic velocities in aqueous solution. Masson (*Phil. Trans.*, 1899, cxcii., A, 331), has succeeded in obtaining satisfactory measurements in gelatin, and for a few ions; Whetham (*Phil. Trans.*, 1893, clxxxiv., A, 337) has made measurements in water. The method now described should be a perfectly general one, as the use of coloured indicator solutions is no longer necessary, and hence the range of ions which may be used as indicators is largely increased.

The method consists in enclosing the liquid to be measured between two partitions of gelatin, which contains the indicator ion in solution; on the passage of the current the cation of the solution is followed by the cation of the indicator, and the anion of the solution by the corresponding anion of the indicator. It is necessary in all cases that these indicator ions should move more slowly than the measured ion.

The position of the boundary between the two solutions is easily seen, on account of the difference in refraction, and the motion is measured by means of a cathetometer. If the above-mentioned condition is fulfilled, the relative velocity of the boundary is not influenced by changing the indicators; thus ($CuSO_4$ and K_2CrO_4), $CuSO_4$ and $NaC_2H_3O_2$), and ($CdSO_4$ and $NaC_2H_3O_2$) all gave the same value for the transport number of $MgSO_4$.

The absolute velocity of a few ions has also been calculated and compared with the velocities found by Kohlrausch, and a very fair agreement is shown to exist between the two sets of measurements.

6. "*Metal-ammonia Compounds in Aqueous Solution.* Part II. *The Absorptive Powers of Dilute Solutions of Salts of the Alkali Metals.*" By H. M. DAWSON and J. MCCRAE.

The influence exerted by the addition of salts of the alkali metals on the distribution of ammonia between water and chloroform at 20° has been investigated. It has been found that so long as the ammonia concentration in the aqueous phase is less than 0·5 normal, the alteration of the distribution coefficient is proportional to the salt concentration; that is, the expression $\frac{k-k'}{n}$ is constant; where k is the distribution coefficient with pure water (26·28), and k' is the observed distribution coefficient with salt solution of normality n. This constant it is proposed to call the "equivalent alteration of the distribution coefficient."

The alteration for each salt is composed additively of two values, one dependent upon the cation, the other upon the anion. Since, according to the views of Abegg and Bodländer, "ammonia-complex formation takes place only with the cation, the differences in the values of the alteration for salts of one metal express the differences in the physical actions of the anions; but differences in the values for salts containing the same anion do not measure the differences in the physical actions of the cations because of the complicating influence of complex formation. The lithium salts show the greatest tendency to form ammonia addition compounds, ammonium salts show it to a less degree, whilst for sodium salts it is probably very small, but greater than for potassium salts.

When the ammonia concentration is greater than 0·5 normal, irregularities occur, and it has been found that

for increasing salt concentration and constant ammonia concentration the value of $\frac{k-k'}{n}$ decreases, whilst for constant salt concentration and increasing ammonia concentration it increases.

Non-electrolytes (urea and cane-sugar) also considerably affect the distribution coefficient, so that Dalton's law is not obeyed.

These results indicate that the solvent power of water is changed to a varying extent by the different ions. The intrinsic property of the ion which is the cause of this difference is not deducible from the ionic theory as it stands at present.

7. "*The Amide, Anilide, and Toluidides (Ortho- and Para-) of Glyceric Acid.*" By P. F. Frankland, F. M. Wharton, and H. Aston.

These compounds have been prepared by the authors with the object of investigating the influence on the rotation produced by replacing the alkoxyl group by the amido-group and its substituted derivatives. After a review of the limited number of cases at present available for ascertaining these relations, the authors pointed out that so far it was observable that if in an homologous series of ethereal salts the rotation is raised by successive additions of CH_2, then the amide has a similar but still higher rotation than the ethereal salts, but that if the successive additions of CH_2 lead to diminished rotation, then the corresponding amide has a lower rotation than the ethereal salts. The first of these relations is exhibited by the derivatives of tartaric, malic, and glyceric acids, whilst the only hitherto known example of the second is furnished by the corresponding derivatives of mandelic acid.

The result of substituting in the amido-group appears in all cases to be an increase in the rotatory effect of the latter. In the case of malic acid, the anilide has a greater molecular rotation than the amide, the *o*-toluidide greater still, and the *p*-toluidide the greatest of all. In the case of glyceric acid, on the other hand, although the anilide has a greater molecular rotation than the amide, the rotation of the *p*-toluidide is less than that of the anilide, and the rotation of the *o*-toluidide is about the same as that of the amide.

The amido-compounds prepared by the authors appear to be the only ones which have hitherto had their rotation determined in the liquid state; in the case of the *o*-toluidide, however, this could unfortunately not be effected, as this, on fusion, at once acquired a strong colour. In consequence of this, the rotation of all the compounds in question was determined also in methyl alcohol solution.

The corresponding compounds of inactive glyceric acid were also prepared, and their melting-points compared with those of the active substances.

Anniversary Dinner.

It has been decided by the Council to arrange for a Dinner of the Fellows of the Society and their friends on Wednesday, March 27th, 1901, the day preceding that fixed for the Annual General Meeting. Further particulars will shortly be announced.

PHYSICAL SOCIETY.

Ordinary Meeting, January 25th, 1901.

Mr. T. H. Blakesley, Vice-President, in the Chair.

It was decided to forward a vote of condolence to His Majesty the King.

The ordinary business of the meeting was postponed.

East London Technical College, People's Palace, E.—Dr. R. A. Lehfeldt will read a paper on "Electro-Chemistry" before the Chemical and Electrical Societies of this Institution, on Wednesday, February 13th, at 6 p.m. Visitors are invited.

CORRESPONDENCE.

THE BRITISH FOOD CONTROL.

To the Editor of the Chemical News.

Sir,—The *British Food Journal*, received on January 26th, contains a list of twelve gentlemen composing the Consulting Scientific Staff of the Austrian Chemical Control.

In the Austrian *Chemiker Zeitung*, No. 2, 1901, published on January 15th, there are two paragraphs relating to the Control. No. 1: "In consequence of well-known events, Dr. Mansfeld (the Secretary) has, on December 10th, 1900, broken off his connection with the European Federation of Permanent Chemical Control, and has dissolved the Austrian Chemical Control." And No. 2: A letter dated January 5th, 1901, signed by Dr. F. W. Dafert, Dr. Max Gruber, T. F. Hanausek, H. Kratschmer, E. Ludwig, Prof. E. Meissl, L. Roesler, F. Strohmer, and A. R. von Vogl, stating that their names have been used in connection with the Chemical Control without their knowledge and consent.

The English organ continues to use the names of these gentlemen in spite of their protest.—I am, &c.,

Hydroxyl.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, del'Académie des Sciences. Vol. cxxxii., No. 1, January 7, 1901.

A New Phosphide of Tungsten.—Ed. Defaçoz.—When copper phosphide is heated with tungsten biphosphide to a temperature of about 1200°, a new crystallised phosphide is obtained. This substance can be easily isolated by treating the mass obtained with dilute nitric acid. The new phosphide is separated in the form of prismatic crystals of a greyish metallic lustre. These have a density of 8·5, and are not attacked by air at ordinary temperatures, but at a red heat are transformed without incandescence into greenish tungstic acid. Analysis shows this substance to have the formula WP.

Some Properties of Sodium Peroxide.—George F. Jaubert.—The author's experiments, described in this paper, are intended to show the inaccuracy of various statements appearing in "Wurtz's Dictionary," with regard to the properties of sodium peroxide. (1). Peroxide of sodium is not pure white in colour, but is of a clear yellow. Many specimens were examined by the author, who found that those which were pure white in colour contained a greater proportion of hydrate or carbonate. Also pure sodium perioxide was prepared by oxidising redistilled metallic sodium in a current of pure dry oxygen. The resulting peroxide was in the form of a yellow powder. The yellow colour darkens on heating. (2). Peroxide of sodium does not deliquesce in the air. In the author's laboratory some peroxide was freely exposed to air for several years without deliquescing. The yellow colour which it possessed at first changed to white, owing to the transformation of the peroxide into carbonate.

Composition of the Hydrate and Nitride of Thorium.—C. Matignon and M. Delépine.—Chydenius announced the existence of a nitride of thorium, produced when ammonia acts on the chloride. M. Moissan obtained this same body by the action of ammonia on the carbide, and one of the authors of the present paper showed that thorium metal combines directly with nitrogen. Finally, Winkler has shown the existence of a hydride of thorium.

The authors now examine these two compounds of thorium with a view to fixing their composition. They are prepared directly from the metal. The results of these experiments show that the hydride has the composition ThH_4 The nitride, which has to be prepared at a somewhat higher temperature, has the formula Th_3N_4. This latter substance is decomposed by water, even in the cold, according to the equation, $Th_3N_4+6H_2O=3ThO_2+4NH_3$.

New Reactions of Organo-metallic Derivatives.—E. E. Blaise.—The author's experiments were performed on zinc compounds for all condensations where ethers of the bromated fatty acids entered into the reaction. In other cases magnesium was used. The reaction of organo-metallic derivatives on the nitriles can be expressed by the general scheme—

$$R-C\equiv N+Br-Mg-R'=R-C\begin{matrix}=N-Mg-Br\\ \diagdown R'\end{matrix}.$$

The ethers of the α-bromated fatty acids react in the same way on the nitriles in presence of zinc—β ketonic ethers being obtained in this case.

$$R=CN+Zn+R'-CHBr-CO_2C_2H_5=$$
$$=R-C\begin{matrix}=N-Zn-Br\\ \diagdown CH(R')-CO_2-C_2H_5\end{matrix}$$
$$\rightarrow R-CO-CH(R)-CO_2C_2H_5.$$

The researches described in this paper lead to new methods of synthesis for ketones, β-ketonic ethers and acids, and perhaps also for α-ketonic acids and bibasic acids. The author is further investigating this matter.

Action of Methylacetylacetone and Ethylacetylacetone on Diazoic Chlorides.—G. Favrel.—Diazoic chlorides react on methylacetylacetone or on ethylacetylacetone with elimination of a molecule of acetic acid and formation of a hydrazone, on account of the union of the diazoic radicle with the remainder of the acetylacetone and subsequent molecular transposition. This reaction is similar to that of cyanacetic ethers with substituted acid radicles and alcoyl acetyl acetic ethers on diazoic chlorides. In all cases the diazoic chlorides behave with regard to these ethers and substituted acetylacetones, in such a manner as to form strong bases which remove the acetyl group.

MISCELLANEOUS.

Messrs. Geo. G. Blackwell, Sons, and Co., Limited, have just issued a small pamphlet on their special refractory bricks and furnace linings. These bricks are particularly advantageous for use in the linings of open hearth and re-heating furnaces for steel, and also for smelting works where lead, copper, silver, spelter, zinc, and other metals are treated. The finest silica bricks will run at a very high temperature, whereas it is claimed that these "refractory" bricks will stand a much higher temperature, and last four or five times as long as the best silica brick made.

The Chemical Composition of Norwegian Tar.—K. Ström.—The tar extracted from the roots of the *Pinus silvestris* is syrupy, with a very acid reaction, reddish-brown in colour, soluble in alcohol, acetone, ether, $CHCl_3$, and C_6H_6; it holds crystals of pimaric acid in suspension. Its density at 15° = 1·0680. It contains 4·70 per cent of volatile acids, 10·94 per cent of phenols, and 60·80 per cent of hydrocarbides. Among the acids may be found formic, acetic, propionic, butyric, valerianic, methylpropylacetic, normal caproïc, œnanthylic, and normal caprylic acid, and probably pelargonic, caprinic, and inactive pimaric acids. Among the phenols are cresol, gaiacol, creosol, ethylgaiacol, propylgaiacol, the two phenols, $C_{11}H_{16}O_2$ and $C_{12}H_{14}O_2$. We find, in fact, 14 per cent of the hydrocarbides in the solid state, and 86 per cent in the liquid state.—*Arch. de Pharm.*, vol. ccxxxvii., p. 525.

NOTES AND QUERIES.

** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Bitumen Compounds.—Can any reader instruct the writer as to finding a suitable place in which to conduct experiments in bitumen compounds? There was a place somewhere in Lambeth that seemed to follow under these lines, but the writer can find no trace of same up to the present time.—W. Macdonald.

MEETINGS FOR THE WEEK.

Monday, 4th.—Society of Arts, 8. (Cantor Lectures). "Elementary Art Education," by J. Liberty Tadd.
—— Royal Institution, 5. General Monthly Meeting.
Tuesday, 5th.—Royal Institution, 3. "Practical Mechanics" (Experimentally treated), by Prof. J. A. Ewing, M.A., F.R.S., M.Inst.C.E.
Wednesday, 6th.—Society of Arts, 8. "Some Experiences of Motor Bicycles," by Joseph Pennell.
—— Royal Institution, 3. "The Government and People of China," by Prof. R. K. Douglas.
Thursday, 7th.—Chemical, 8. Ballot for the election of Fellows. "The Action of Hydrogen Bromide on Carbohydrates," by H. J. H. Fenton and Mildred Gostling. "Note on a Method of Comparing the Affinity-Values of Acids," by H. J. H. Fenton and H. O. Jones. "Organic Derivatives of Phosphoryl Chloride, and the Space Configuration of the Valencies of Phosphorus," by R. M. Caven. "Synthetical Work with Sodamide Derivatives," "Note on Two Molecular Compounds of Acetamide," and "Diacetamide—a New Method of Preparation," by A. W. Titherley, M.Sc., Ph.D.
—— Royal Institution, 3. "Society in France before before the Revolution," by the Rev. Henry Grey Graham.
Friday, 8th.—Royal Institution, 9. "History and Progress of Aerial Locomotion," by Prof. G. H. Bryan, F.R.S.
—— Physical, 5. (Annual General Meeting). Address by the President. "A Mica Echelon Grating," by Prof. R. W. Wood.
Saturday, 9th.—Royal Institution, 3. "Vocal Music, its Growth and Decay," by F. Corder, F.R.A.M.

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THE CHEMICAL NEWS.

VOL. LXXXIII., No. 2150.

ON THE PRESENCE OF ARSENIC IN VARIOUS COMMERCIAL PRODUCTS.

By Dr. T. L. PHIPSON.

As early as 1862 I found notable amounts of arsenic and selenium in the sulphur of the Solfatare, near Naples (*Comptes Rendus*, 1862). This sulphur was purchased for pharmaceutical use in Belgium.

Since then I have examined some specimens of Sicilian sulphur and artificial English sulphur (from soda refuse), which were quite exempt from arsenic.

The volcanic sulphur of Hecla, which I examined in 1870, gave mere traces of arsenic.

Many phosphates used in pharmacy will be found to yield arsenic when carefully examined, and doubtless arsenic thus finds its way into phosphatic syrups and other medicaments.

The pyrites used in the manufacture of sulphuric acid almost invariably yield a certain quantity of arsenic (often 0·1 per cent, or more), and chamber acid in which impurities of various kinds, such as lead, mercury, thallium, selenium, and arsenic, are concentrated, is, of course, quite unfit for the production of phosphoric acid or glucose, or for any use connected with food or medicaments. Some specimens of this chamber acid have yielded as much as 1·44 per cent of arsenious acid.

M. Herz, an apothecary of Berlin, detected arsenic in the phosphoric acid used in pharmacy as early as 1834. This phosphoric acid was prepared by acting upon phosphorus by nitric acid. Its solution, treated by sulphuretted hydrogen, gave a deposit of the yellow sulphide of arsenic after being allowed to stand for some days. The same result was obtained at the same time by Mr. Barwald, who got 8 grains of sulphide of arsenic from 1 pound of phosphoric acid; isolated the arsenic itself, proved that the latter did not come from the vessels used, nor the nitric acid, nor the sulphuretted hydrogen, but from the phosphorus. He then examined the phosphorus purchased at several other pharmacies in Berlin with the same results.

About the same time Justus von Liebig obtained similar results with specimens of phosphorus purchased at several drug-stores in Frankfurt-a-M.

ARSENIC IN BEER.

By JOHN RYDER and ALFRED GREENWOOD, M.D., D.P.H.

HAVING had occasion during the last two months to examine a number of samples of beer for arsenic, the following method was used in those cases in which the quantity of arsenic present was determined:—

Take 2 litres of beer (or less, according to the sublimate of crystals obtained in the qualitative test), and boil down to 1000 c.c. Then add 3 or 4 grms. of bright copper foil in small pieces (about ½ inch square) and one-sixth litre of pure re-distilled HCl (sp. gr. 1·16). Boil for one hour. Pour beer into another beaker containing about 1 grm. bright copper foil, and boil for a quarter of an hour longer. If no stain on this copper, the beer may be put aside. Wash the copper from the two treatments with distilled water, transfer to porcelain basin, dissolve in 20 c.c. HNO_3 (sp. gr. 1·42), evaporate off excess of acid.

(From this stage the method is that described in Blair's "Chemical Analysis of Iron" (Second Edition, p. 189) for the determination of small quantities of arsenic in iron and steel).

Add 20 c.c. H_2SO_4 (sp. gr. 1·84), heat to dryness on sand-bath until H_2SO_4 fumes come off, transfer residue to distillation flask, add 7½ grms. pure $FeSO_4$ cryst. (B.P. granulats), and fit cork with tubes attached.

Now add down funnel 75 c.c. pure re-distilled HCl (sp. gr. 1·16), and distil into 150 c.c. distilled H_2O until delivery tube is too hot to bear the hand; then change receiver for beaker containing 50 c.c. distilled H_2O, and continue distillation for five minutes.*

Heat the two receivers to about 70° C., pass brisk current of H_2S through each for ten minutes, digest on water-bath for ten minutes, and then pass H_2S through again for ten minutes. Place on water-bath. After a while the As_2S_3 will settle well, leaving the supernatant liquid clear and colourless. Now bubble CO_2 through to dispel H_2S, filter off As_2S_3, wash with H_2O, then alcohol, CS_2—to dissolve out any free S—alcohol, and H_2O.

Dissolve the As_2S_3 in cold dilute AmHO (1 : 4), letting the ammoniacal solution run into a weighed porcelain crucible. Evaporate to dryness on water-bath, and dry in oven (until constant) at 100° C.

In iron and steel analysis, when taking 5 grms. sample and using above quantities, 0·016 per cent As may be determined, so that when taking 2 litres of beer the same weight of precipitate would represent 0·00004 per cent arsenic.

Health Department, Municipal Offices,
Earle Street, Crewe, Feb. 1, 1901.

SULPHOCYANIDES OF POTASSIUM AND SODIUM.
ON A PECULIAR BLUE COLOUR PRODUCED WHEN THESE SALTS ARE HEATED.

By W. B. GILES, F.I.C.

SOME time ago when making experiments on the reducing action of cyanide of potassium on titanic acid, and some other oxides, it occurred to me to see what would happen if sulphocyanide of potassium was substituted for the cyanide. On fusing small quantities of the sulphocyanide with the oxides in porcelain crucibles I noticed that a very intense blue colour was produced at a red heat, and I conceived at first that this was due to some reduction of the oxides, and that it might afford a good means for their detection. On pursuing the matter further I found, however, that pure silica yielded just the same intense blue colour with the sulphocyanide when they were heated to redness together. Then I tried heating the sulphocyanide by itself, and found that without any addition whatever it also yielded this colouration. Not being able to find any account of this peculiar behaviour of the salt, I thought possibly that there might be something unusual in the sample of sulphocyanide of potassium I was using. To settle this question I obtained five more samples of pure sulphocyanide of potassium, and three samples of pure sulphocyanide of sodium, from different sources. The whole of these eight samples with one exception (which is referred to later on), gave the blue colouration on heating in a very marked manner. In order to obtain this curious result it is merely necessary to heat in a porcelain crucible over a Bunsen burner a small amount of the *pure* salts, using a gentle heat till all the adherent moisture is expelled; then on raising the heat slowly the salt becomes slightly pink or yellow, and when an incipient red heat is reached begins to darken, and a very bright blue colour is produced, which becomes more intense as the heat is

* This second receiver very seldom contains even a trace of arsenic, but it is best to use it as a safeguard.

raised, till sometimes it appears nearly black. A remarkable feature is that the colour only persists at a strong heat; directly the lamp is withdrawn the colour begins to fade, and if the salt has not been heated too strongly, long before solidification takes place, the mass is quite white again. On re-heating the salt the colour again appears, and with care this can be repeated a great number of times. As, however, heating in crucibles entails oxidation, and the salt often takes fire, small test-tubes made of hard combustion glass are substituted with advantage. On heating the sulphocyanide in tubes it is seen that small quantities of sulphur sublime. Yet after eight or ten careful reproductions of the colour by alternate heating and cooling have been made on a small quantity, the residue on examination appears to consist principally of unaltered sulphocyanide. The cause of the colouration is evidently connected with sulphur, for if some of the salt is heated to such a point that the blue colouration is just perceptible, and a small chip of sulphur is introduced, a very marked increase of the colour is noticed. If, however, too much sulphur is added the colour is destroyed. When pure sulphocyanide of potassium or sodium is heated in a current of dry hydrogen it does not prevent the formation of the blue colour, but after the current of gas has been passed for a long time, the colour fades away gradually, and the salt becomes white again, or nearly so. If the sulphocyanides are pure the escaping gas contains a large amount of hydric sulphide, and the residue in the tube consists principally, if not wholly, of potassium cyanide, $KCyS + H_2 = KCy + H_2S$. If, however, the sulphocyanides contain certain impurities, such as carbonate or hydrate of potassium, the formation of the blue colour is entirely prevented, and, on heating in hydrogen, ammonia is given off as well as hydric sulphide. I have mentioned previously that one sample of the sulphocyanide of potassium, though marked as "pure," did not yield any blue colour on heating, either in a test-tube or in dry hydrogen. The cause of this was found to be that it was strongly contaminated with carbonate of potassium. This sample gave a deep yellow or orange-colour on heating it, and behaved quite differently to the pure samples. Pure sulphocyanides are perfectly indifferent to phenolphthalein, whereas this sample was strongly alkaline. If instead of starting with the sulphocyanides themselves, *pure* cyanide of potassium is fused in a tube of hard glass and small quantities at a time of sulphur are added, by careful manipulation it is possible to produce the blue colouration in a very distinct manner. But if the cyanide is impure (and what has been kept for any time almost always contains carbonate), or if too much sulphur is added, the colour is not obtained. It is difficult to explain the formation of this blue compound; the sulphocyanides on heating seem to be (at least in part) dissociated, as appears from the slight sublimation of free sulphur, and while the blue colour is clearly due in some way to sulphur an excess destroys it. In this connection it may be of interest to note that the temperature at which the blue colouration manifests itself (a dull red heat) is about the point at which the vapour density of sulphur changes from 96 to 32 as referred to hydrogen, or from a six atom molecule to a two atom molecule, according to Mendeleeff.

It would be of interest to know whether Sir William Crookes, who has worked so much with the seleniocyanides, has ever noticed any analogous colouration when seleniocyanide of potassium, for instance, is heated.

Compounds of Boron Bromide with Phosphorus Chlorides.—M. Tarible.—Boron bromide in presence of chloride of phosphorus reacts very easily, giving double compounds. The substances thus obtained are perfectly crystalline, and are decomposed by water in the cold, chlorine and ammonia gas being produced. In all cases their formulæ are different from those compounds which are obtained with phosphorus bromide.—*Comptes Rendus*, cxxxii., No. 2.

NEW METHOD FOR THE ESTIMATION OF TANNING MATERIALS.

By L. SPECHT and F. LORENZ.

This method depends on the precipitation of safranine in the form of ammonio-tannic lake, and on the reducing action exercised by hyposulphite on safranine. The tanning material is precipitated by tartar emetic and safranine, the excess of which is titrated with hyposulphite. The strength of this latter is found by means of pure safranine. The number of c.c. used indicates the amount of safranine that has not taken part in the reaction, and the difference between this figure and that obtained with the amount originally required enables us to estimate the quantity of safranine necessary to form the lake, and, consequently, the strength of the tanning material. To be able to express this relative value in figures, it is necessary to titrate a tannin of well-known composition, under the same conditions.

The large number of experiments we have carried out to test the value of our process have given results of an entirely satisfactory character.

As a standard tannin of 100 per cent we used tannic acid dried at 100°, Ph. G. III., supplied by Schering and Co., Berlin.

The T safranine, from the Badische Anilin und Soda Fabrik, of which we made use, was first purified by repeated crystallisations in alcohol. To diminish the oxidising action of the oxygen dissolved in the water as much as possible, we always used boiled water. Instead of hyposulphite of sodium, we used hyposulphite of ammonium, which is much more stable. To prepare this reagent we made a mixture of 50 grms. of zinc powder and 100 grms. of water, and added to this 600 c.c. of a solution of bisulphite of ammonium at 20° B., and neutralised with ammonia. During this operation it is important that the temperature should not exceed 36°.

After standing, 75 c.c. of the clear liquid were taken and poured into 2 litres of water. A flocculent precipitate separates, which is allowed to settle, and the liquid is then covered with a layer of mineral oil, to protect it from the oxygen of the air.

The end of the titration is taken as the moment when complete decolouration takes place.—*Chemiker Zeitung*, 1900, p. 170.

ON THE COMPOUNDS OF TELLURIC ACID WITH THE IODATES.

By R. F. WEINLAND and H. PRAUSE.

Among the compounds of the iodates and the acids of the sixth group of elements, we know up to the present only those of sulphuric acid, chromic acid, molybdic acid, and tungstic acid. Taking the first of these acids as an example, the different forms which exist are as follows:—$I_2O_5.2SO_3.2K_2O.H_2O$; $I_2O_5.SO_3.K_2O$; $2I_2O_5.8SO_3.5K_2O$. In this paper the authors examine a series of new salts formed by the union of telluric acid with the iodates.

Monoiodotellurate of Potassium, $I_2O_5.2TeO_3.K_2O.6H_2O$. —This salt is formed when we allow an aqueous solution of the three oxides to evaporate slowly at the ordinary temperature. It crystallises in flattened colourless prisms. The solutions it gives with water have an acid reaction; when submitted to the action of heat this body loses the greater part of its water of crystallisation at 100°, but the remainder only at 250°.

Monoiodotellurate of Rubidium, $I_2O_5.2TeO_3.Rb_2O.6H_2O$. —This salt is obtained by the evaporation of solutions containing a quantity of telluric acid, slightly higher than that required by the formula. This salt crystallises in prisms analogous to those of the above mentioned potassium salt.

Monoiodotellurate of Ammonium,—

$I_2O_5.2TeO_3.(NH_4)_2O.8H_2O$.

—This body consists of colourless flattened crystals, which attain a diameter of 1·5 c.m. They contain 8 molecules of water of crystallisation.

Di-iodotellurate of Potassium, $I_2O_5.TeO_3.K_2O.8H_2O$.—This body is prepared from an aqueous solution of 2 molecules of IO_3H, 1 molecule of TeO_4H_2, and 2 molecules of KOH. The liquor should have a slightly acid reaction. The di-iodotellurate is also formed in good proportion, by evaporating aqueous solutions of iodic acid, telluric acid, and potash mixed together in the proportions of 3 : 1 : 3·2. This salt occurs in the form of rhombohedric crystals having a vitreous lustre. Like the monoiodotellurate, it loses the whole of its water at 250°. —*Berichte*, vol. xxxiii., p. 1015.

A BIBLIOGRAPHY OF STEEL WORKS ANALYSIS.

PART VII.

By HARRY BREARLEY.

(Continued from p. 54).

CHROMIUM (*continued*).

IV. Means of Converting to Chromic Acid.

IV.*a*. *In the Dry Way*.—

1043. Clarke (*C. N.*, xvii., 232).—Chromite (and other refractory materials) is fused with soda fluoride and bisulphate, and oxidised with hypochlorite; or at once by including KNO_3 in the fusion. CrO_3 not completely separated from Fe and Al by Na_2CO_3.

1044. Namias (*J. S. C. I.*, 1891, 486).—Fuse ore with $KHSO_4$, precipitate water extract with MgO, and fuse with $KClO_3+NaKCO_3$.

1045. Moissan (*C. N.*, lxvii., 137).—Powdered chromeisen is converted to CrO_3 by melting with KNO_3.

1046. Kayser (*C. N.*, xxxvi., 153).—Heat chrome-iron with a mixture of Na_2CO_3 and CaO.

1047. Pemberton (*C. N.*, lxiii., 241).—Chromite and Na_2CO_3 are heated over night by a Bunsen, and next morning over the blast. Decomposition is complete.

1048. Haussermann (*J. S. C. I.*, 1892, 182).—Fuse powdered ore with K_2CO_3 and NaHO.

1049. Massignon and Vatel (*C. N.*, lxiii., 273).—Heat ore mixed with $CaCl_2$ and CaO (or $CaCO_3$).

1050. Clark (*J. S. C. I.*, 1892, 501).—Ferro-chromium is not completely dissolved by H_2SO_4 (1073). Oxidise with MgO or CaO+NaHO. FeCr is decomposed by heating with $Ca(HO)_2$, or in the vapour of S or CS_2. Latter process available for steels.

1051. Donath (*J. I. S. I.*, 1887, ii., 371).—Heat with barium peroxide, and extract CrO_3 with acidulated water.

1052. Kennicut and Patterson (*J. C. S.*, lx., 366).—Fuse with barium peroxide and Na_2CO_3, dissolve in HCl, re-oxidise with alkaline H_2O_2, acidify, and titrate.

1053. Clark (*J. C. S.*, lxiii., 1081).—FeCr and chromite are completely decomposed by Na_2O_2. Heat to make pasty, not to liquefy. Na_2O_2 does not separate Fe and Cr.

1054. Reinhardt (*J. I. S. I.*, 1890, i., 375).—Fuse with soda-lime and $KClO_3$. Titrate with $FeSO_4$.

1055. Smith (*C. N.*, lxiv., 44 and 218).—An electric current passed through molten potash containing chromiferous material completely oxidises it to CrO_3. Titrate with $FeSO_4$.

IV.*b*. *Conversion to* CrO_3 *in the Wet Way*.—

1056. Storer (*C. N.*, xxi., 198).—Strongly ignited Cr_2O_3 and chromite are converted to CrO_3 by boiling with HNO_3+KClO_3. Precipitated as $BaCrO_4$.

1057. Stoddart (*C. N.*, xxiii., 284).—Storer's process does not completely decompose chromite.

1058. Phillips (*C. N.*, xxix., 28).—Decompose chromeisen with H_2SO_4 in closed tubes, oxidise with Na_2CO_3 and Br. Zn, Mn, Fe, and Al are completely separated (see 1043).

1059. Marchal and Wiernich (*J. S. C. I.*, 1891, 1034).—To nearly neutral H_2SO_4 solution, add MnO_2 and boil; Fe is precipitated. Precipitate Al with AmHO, reduce CrO_3, and precipitate.

1060. Matignon (*J. C. S.*, l., 984).—In alkaline solutions H_2O_2 immediately converts Cr_2O_3 to CrO_3; in acid solutions the easily decomposable perchromic acid is formed.

V. Detection of Chromium.

1061. Storer (*C. N.*, i., 253, &c.).—PbO_2 best reagent for effecting oxidation. PbO_2, MnO_2, and $KMnO_4$ form CrO_3 in cold acid solutions; PbO_2 (not Pb_3O_4), MnO_2, $KMnO_4$, Br, I, HgO, and hypochlorite in alkaline solutions. Formation of perchromic acid with H_2O_2 the most delicate reaction.

1062. Neville (*C. N.*, xxxiv., 19).—Add ether and H_2O_2 to CrO_3 solution; a blue colour = Cr. Ni, Co, Fe, Mn, and Al do not interfere; acetates do. The blue colour in ether is used as indicator (McCulloch, *C. N.*, lv., 2) in estimating acidimetrically K_2CrO_4 in the presence of $K_2Cr_2O_7$.

1063. Donath (*C. N.*, lix., 109).—Similar to 1029. Use KI and starch. Small quantities are estimated by precipitating with Am_2S.

1064. McCay (*C. N.*, lxv., 221).—After fusing with $Na_2CO_3+KNO_3$ the yellow colour of the acidified extract looked for may have been destroyed by the nitrous acid present (see 971).

1065. Terriel (*C. N.*, xi., 136).—Precipitate the ferric solution with KHO, oxidise with permanganate, and add lead acetate and acetic acid to the filtrate. Traces of W, Mo, and Va in steel are similarly detected.

1066. Walden (*J. C. S.*, liv., 321).—Diphenylamine in concentrated H_2SO_4 detects 1 part $K_2Cr_2O_7$ in 700,000.

VI. Miscellaneous Notes.

1067. Fresenius and Hintz (*C. N.*, lxi., 65).—Scheme for very elaborate analysis of chrome-iron. The material is decomposed in a current of chlorine.

1068. Clark (*J. S. C. I.*, 1895, 510).—Decompose ore with $KHSO_4$ preparatory to estimation of SiO_2, CaO, MgO, Fe_2O_3, Al_2O_3, and Cr_2O_3.

1069. Moissan (*C. N.*, lxx., 93).—Preparation, physical and chemical properties of metallic Cr.

1070. Jannasch and Vogtherr (*C. N.*, lxiv., 293).—Chromite decomposed with HCl in sealed tube.

1071. Schneider (*J. I. S. I.*, 1886, 399).—Fifty per cent FeCr would dissolve in HCl if it were not for a protective coating of oily hydrocarbon.

1072. Rideal and Rosenblum (*C. N.*, lxxiii., 1).—Give prominence to Na_2O_2 in a review of the means proposed for decomposing chromite, ferro-chromium, &c. A bibliography of forty items.

1073. Warren (*C. N.*, lxv., 186).—Ferro-chromium is completely dissolved by hot concentrated H_2SO_4 (see 1050). Borax in fusion mixtures contaminates the precipitates of the subsequent analysis.

1074. Carnot and Goutal (*J. C. S.*, lxxii., ii., 555).—Chromium exists in steel as a Cr-Fe carbide.

1075. ZIEGLER (*J. S. C. I.*, 1893, 377) —Describes the following processes for steel :—Fusion of the dried residue; removal of the iron with cupram-monium chloride; fusion with $NaHSO_4$, or oxidation with $KMnO_4$; and dissolving out other chlorides than Cr from the dried residue with alcohol.

1076. PROCTOR (*J. S. C. I.*, 1897, 413).—A review of the processes for estimating CrO_3 and some mixtures of Cr salts.

1077. JERVIS (*C. N.*, lxxvii., 133).—Either acid or alkaline chromate solutions are reduced by filter-paper (see 987).

1078. PARRY and MORGAN (*C. N.*, lxvii., 307).—There is no satisfactory process for estimating Cr in steel. Describe some processes the like of which are otherwise noticed.

(END OF PART VII.).

CONCERNING LIPASE, THE FAT-SPLITTING ENZYME, AND THE REVERSIBILITY OF ITS ACTION.*

By J. H. KASTLE and A. S. LOEVENHART.

IT was suggested by one of us (Loevenhart), that possibly lipase might be capable of effecting the synthesis of fats from fatty acid and glycerin as well as their hydrolysis into these products. It was with the view of making an experimental study of this question that this investigation was first undertaken. An examination of the literature of the subject revealed that but comparatively little was known concerning the fat-splitting enzyme. It was therefore deemed advisable to extend the original scope of the investigation. The most convenient source of the enzyme to us was the pancreas of the pig. In the preparation of our extracts, the organ was removed from the animal within thirty minutes after death, dissected as free as possible from fat, thoroughly macerated with coarse white sand, and extracted with water or glycerin. It was afterwards found more convenient, however, to cut up the pancreas in small pieces upon its removal from the animal, and preserve it in chloroform water in cold storage until required for use. At first the activity of the enzyme was tested upon pure butter-fat, litmus being used as the indicator, and the time being noted that was required to pass from the blue colour to a definite shade of red. Under the best conditions, however, lipase hydrolyses the fats but slowly, and hence they are by no means convenient substances with which to follow the change in question. In testing the activity of the pancreas extract on other ethereal salts, it was observed that it hydrolysed ethyl butyrate comparatively rapidly, and, except where expressly stated to the contrary, this ethereal salt was employed in all of our experiments. Ethyl butyrate further possesses the advantage that the amount split by water alone at the temperature at which we worked, is not measurable within the duration of our experiments. The experiments were carried out in test-tubes usually in the following manner :—4 c.c. of water, 0·1 c.c. toluene (as antiseptic), and 0·26 c.c. ethyl butyrate† were placed in test-tubes. The tubes were then tightly corked and heated to the desired temperature, usually 40°, for five minutes, to bring their contents to the temperature of the bath, at the end of which time 1 c.c. of the enzyme solution was added to each. The tube was then heated for the desired time, usually for fifteen minutes, when it was removed from the bath, plunged into ice-water, and titrated with N/20 KOH, neutral litmus being used as the indicator. In what follows, the initial acidity of the enzyme solution, usually amounting to 0·1 to 0·2 c.c. N/20 KOH, has in every case been deducted from the c.c. KOH required.

That the hydrolysis of ethyl butyrate and other ethereal salts was in reality brought about by the action of an enzyme, and not by other agents, was proved by numerous control experiments in which the solution of the enzyme was boiled before it was used. It may be of interest to note in this connection that in not a single instance did the control experiment show any hydrolysis of the ethereal salt.

The action of fat-splitting bacteria was prevented by antiseptics, usually toluene or thymol.

In our early experiments no special attention was paid to the amount of pancreas employed in the preparation of the extracts. It soon became manifest, however, that it would be far better, for purposes of comparison at least, to employ definite amounts of the gland, and hence it will be observed in what follows that 10, 20, and even 50 per cent extracts were used. By this is meant that 10, 20, or 50 grms. of gland were extracted with water, and made up to 100 c.c.

Several other tissues of the pig have been found to exhibit lipolytic activity towards ethyl butyrate, notably the liver, the submaxillary gland, and the kidney. A comparison of the lipolytic activity of 10 per cent extracts of these tissues has been made in the following manner :—Tubes were prepared containing 4 c.c. of water, 0·1 c.c. toluene, and 0·26 c.c. ethyl butyrate. These were then heated for five minutes at 40°, when 1 c.c. of the extract to be tested was added. The enzyme was allowed to act for forty minutes, at the end of which time the solution was titrated with N/20 KOH. The following were the results obtained :—

	c.c. N/20 KOH required.	Per cent of hydrolysis.
Pancreas	1·4	3·52
Kidney	0·7	1·76
Liver	4·1	10·29
Submaxillary gland	0·5	1·26

Taking the extract of the pancreas as unity, the lipolytic activity of the other tissues of the pig stand in the following ratio :—

Pancreas	1·0
Liver	2·93
Kidney	0·50
Submaxillary gland	0·36

The liver of the pig showed such remarkable lipolytic activity that it occurred to us to compare it with the liver of certain other animals in this respect. Livers of the pig, beef, sheep, chicken, and duck were obtained in fresh condition in the market. 10 per cent aqueous extracts of these were prepared, and their activity toward ethyl butyrate tested in the manner already described.

Duration of experiments, fifteen minutes; temperature, 40°; antiseptic, toluene.

	c.c. N/20 KOH required.	Per cent of hydrolysis.
Pig liver	3·45	8·66
Sheep ,,	1·90	4·77
Duck ,,	1·075	2·70
Beef ,,	0·875	2·20
Chicken ,,	0·775	1·95

Another interesting occurrence of lipase has been observed in the stomach of the pig. It has long been known that fats are hydrolysed to some extent in the stomach (Marcet, *Proc. Roy. Soc.*, 1858, ix., 306; Ogata, *Du Bois Arch.*, 1881, 515; Cash, *Arch. f. Anat. u. Physiol*, 1880, S. 323). The exact cause of this, however, seems not to have been determined with certainty. By some it is believed to be brought about by bacteria in the early stages of gastric digestion (Shäfer, "Text-book of Physiology," 1898, vol. i., p. 443). In order to test this point, 25 grms.

* From the *American Chemical Journal*, xxiv., No. 6.

† At 30° C. (summer temperature), 0·26 c.c. ethyl butyrate weighs 0·2300 grm. This quantity, if completely hydrolysed, would require 39·7 c.c. N/20 KOH. These numbers are employed in the following in calculating the amount of hydrolysis.

of the mucous membrane of the pig's stomach were ground with coarse sand, and water added. The extract was strained through linen cloth, and made up to 100 c.c. A small quantity of toluene was added as the antiseptic. This extract was found to possess lipolytic activity in neutral solutions. It was found to be rendered permanently inactive, however, by free hydrochloric acid in about the quantity normally present in gastric juice. These facts are brought out in the following experiments:—

In the first series of experiments three solutions were employed, labelled A, B, and C, respectively. Solution A contained 5 c.c. of 0·6 per cent hydrochloric acid, and 5 c.c. of the active extract of the pig's stomach. The hydrochloric acid was therefore acting in a concentration of 0·3 per cent.

Solution B contained 5 c.c. of the active extract of the pig's stomach and 5 c.c. of water. Solution C contained 5 c.c. of hydrochloric acid of 0·6 per cent, and 5 c.c. of water.

Experiments (First Series).

Time, thirty minutes; temperature, 40°.

(1). 1 c.c. solution A; 4 c.c. water; 0·1 c.c. toluene; 0·26 c.c. ethyl butyrate.
Increase in acidity = 0·05 c.c. N/20 KOH = 0·13 per cent hydrolysis.

(2). A duplicate experiment of above (No. 1), gave the same result. This slight hydrolysis was due to the hydrochloric acid present; see Exp. 4.

(3). 1 c.c. of solution B; 4 c.c. water; 0·1 c.c. toluene; 0·26 c.c. ethyl butyrate.
Increase in acidity = 0·25 c.c. N/20 KOH = 0·64 per cent hydrolysis.

(4). 1 c.c. solution C; 4 c.c. water; 0·1 c.c. toluene; 0·26 c.c. ethyl butyrate.
Increase in acidity = 0·05 c.c. N/20 KOH; decomposition, 0·13 per cent.

Experiments (Second Series).

Time, thirty minutes; temperature, 40° C.

(1). 2 c.c. extract of pig's stomach (boiled); 2 c.c. water; 0·1 c.c. toluene; 0·26 c.c. ethyl butyrate.
Increase in acidity 0·1 c.c. N/20 KOH; decomposition, 0·25 per cent.

(2). 2 c.c. extract pig's stomach (boiled); 2 c.c. 0·6 per cent hydrochloric acid; 0·1 c.c. toluene; 0·26 c.c. ethyl butyrate.
Increase in acidity 0·2 c.c. N/20 KOH; decomposition, 0·5 per cent

(3). 2 c.c. active extract of pig's stomach; 2 c.c. 0·6 per cent hydrochloric acid; 0·1 c.c. toluene; 0·26 c.c. ethyl butyrate.
Increase in acidity 0·1 c.c. N/20 KOH; decomposition, 0·25 per cent.

(4). 2 c.c. active extract of pig's stomach; 2 c.c. water; 0·1 c.c. toluene; 0·26 c.c. ethyl butyrate.
Increase of acidity 0·8 c.c. N/20 KOH; decomposition, 2 per cent.

These experiments certainly show that while a lipolytic enzyme is present in extracts of the mucosa of the stomach, it cannot effect the hydrolysis of fats in the presence of 0·3 per cent hydrochloric acid, and hence any hydrolysis of fats brought about by it in the stomach would probably be confined to the first stages of gastric digestion. The following experiments show further that this enzyme is rendered permanently inactive by hydrochloric acid of this strength, proving therefore that on passing from the stomach into the intestine, the enzyme does not again become active.

Experiments (Third Series).

(1). 2 c.c. active extract of pig's stomach; 2 c.c. 0·6 per cent hydrochloric acid; 0·1 c.c. toluene.
This mixture was heated ten minutes at 40°, when 0·2 c.c. of litmus solution was added, and the contents of the tube just neutralised with N/20 KOH. 0·26 c.c. ethyl butyrate was then added, and the tube again placed in the bath at 40°. The solution remained neutral permanently.

(2). Repetition of the above gave the same result.

(3). 2 c.c. active extract pig's stomach; 2 c.c. water; 0·1 c.c. toluene.
This mixture was heated for ten minutes at 40°, when 0·2 c.c. of litmus solution, 6·8 c.c. water,* and 0·26 c.c. of ethyl butyrate were added. The tube was then again placed in the bath at 40°. The solution became red in five minutes. After heating for twenty-five minutes, it required 0·7 c.c. N/20 KOH; decomposition, 1·76 per cent. When returned to the bath, after neutralisation, it became red again almost immediately. These experiments were repeated with extracts made from the stomach of a second animal with like results.

Still another occurrence of lipase, of doubtless great physiological interest, has been found in the small intestine of the pig. A short section of the intestine, including the duodenum and upper part of the jejunum, was thoroughly cleansed in running water. At the time the animal was killed a small quantity of fluid was found in the small intestines. After cleansing, the mucosa was scraped off, and macerated with coarse white sand, and extracted with water. A 10 per cent extract was thus prepared. This extract was quite similar in appearance to the pancreatic extracts. Tubes were prepared containing 4 c.c. of water, 0·1 c.c. toluene, and 0·26 c.c. ethyl butyrate. They were then heated in the bath at 40° for five minutes, at the end of which time 1 c.c. of the active or boiled extract was added, after which the tubes were heated for fifteen or thirty minutes. The following results were obtained:—

	Time in minutes.	C.c. N/20 KOH required.	Per cent of hydrolysis.
1	15	0·9	2·26
2	30	1·65	4·14
*3	15	1·00	2·51
4	30	1·30	3·26

* In Experiments 3 and 4, 0·1 grm. thymol was used as the antiseptic.

The boiled extract showed no activity whatever.

According to these results, the mucous lining of the small intestine possesses a lipolytic activity equal to three-fourths that of the fresh pancreas for equal amounts of tissue. The probable physiological significance of this fact will be briefly discussed in a subsequent part of this paper.

Effect of Filtration.

In our earlier work with the enzyme, the attempt was made to obtain it in the form of a clear solution, free from all suspended matter of any kind. By repeated filtration we succeeded in obtaining clear solutions, showing only a slight opalescence. Unfortunately, such solutions were always found to be exceedingly weak in lipolytic power. On the other hand, it was found that if the pancreas was thoroughly macerated with sand, and the macerated mass thoroughly mixed with water, and simply strained through linen or cotton cloth, an extract of great lipolytic power was obtained. The effect of filtration was invariably to diminish the activity of the solutions. This was proved experimentally for aqueous and glycerin extracts of both the pancreas and liver. The same was also found to hold for the pancreatin of Parke, Davis, and Co. A 2 per cent solution of this preparation is yellowish in colour, and is turbid. In this shape it possesses weak but measurable lipolytic power. On filtering a great many times a clear yellow solution is obtained, which possesses only a trace

* This quantity of water was added in order to make the concentration the same as in Experiment 1.

of its original lipolytic activity. To show the effect of filtration on the liver extract, the following experiments are cited:—Before filtering, 1 c.c. of a 10 per cent liver extract was found to hydrolyse 6·28 per cent of ethyl butyrate in fifteen minutes at 40°. After filtering repeatedly through the same filter-paper, it hydrolysed only 2·76 per cent of ethyl butyrate under the same conditions, showing a falling off in activity of over one-half as the result of filtration.* The removal of lipase, along with the suspended matter in the solution, was observed in still another connection. When an active pancreatic extract acts on ethyl butyrate at 40°, the butyric acid produced soon coagulates the proteids in the extract. On filtering, it was found that the clear filtrate possessed little or no lipolytic power, whereas the proteid coagulum was found to be exceedingly active. In view therefore of the injurious effect of prolonged filtration, it was deemed advisable to employ extracts which had been prepared in the manner above described, and which had simply been strained through linen or cotton cloth. Care was taken, however, to macerate thoroughly.

(To be continued).

SOME PRINCIPLES AND METHODS OF ROCK ANALYSIS.†

By W. F. HILLEBRAND.

Part I.—Introduction.

I. *Importance of Complete and Thorough Analyses.*

The composition of the ultimate ingredients of the earth's crust—the different mineral species which are there found and of many of which its rocks are made up—was the favourite theme of the great workers in chemistry of the earlier half of this century, and for the painstaking care and accuracy of Berzelius, Wöhler, and others the mineralogists and geologists of to-day have need to be thankful. Considering the limited facilities at their disposal in the way of laboratory equipment and quality of reagents, the general excellence of their work is little short of marvellous. As an outgrowth of and closely associated with the analysis of minerals came that of the more or less complex mixtures of them—the rocks—to aid whose study by the petrographer and geologist a host of chemists have for many decades annually turned out hundreds of analyses of all grades of quality and completeness. With the growth and extraordinary development of the so-called organic chemistry inorganic chemistry gradually fell into a sort of disfavour. In many, even the best, European laboratories, the course in mineral analysis, while maintained as a part of the curriculum of study, became but a subordinate prelude to the ever-expanding study of the carbon compounds, whose rapid multiplication, offering an easy and convenient field for original research and possible profit, proved a more tempting opening to young chemists than the often-worked-over and apparently exhausted inorganic pasture. For one student devoting his time to higher research on inorganic lines were perhaps fifty engaged in erecting the present enormous structure of carbon chemistry. The instruction afforded the student in mineral analysis was confined to the ordinary separations of the commoner ingredients occurring in appreciable quantities, with little regard to supposed traces, and with still less attempt to find out if the tabulated list really comprised all that the mineral or rock contained.

With the introduction of improved methods of examination by the petrographer, especially as applied to thin rock sections, and the use of heavy solutions, whereby, on the one hand, the qualitative mineral composition of a rock could be preliminarily ascertained with considerable certainty, and on the other, chemical examination of the more or less perfectly separated ingredients was rendered possible, a great help and incentive was afforded to the few chemists engaged in rock analysis. The microscope often obviated in part the necessity for tedious and time-wasting qualitative tests, and the heavy solutions, by permitting the concentration and separation of certain components, facilitated the detection of elements whose existence had long been overlooked.

Meanwhile in the progress of chemistry new methods and reagents for qualitative detection and quantitative separation and estimation were gradually being discovered and devised. The supposed adequacy of some well-established methods was shown to be unwarranted; some had to be discarded altogether; others were still utilisable after modification. In the light thus shed it became possible to explain many hitherto incomprehensible variations in the composition of some rock species or types, as shown in earlier analyses, and in not a few cases it appeared that the failure to report the presence of one or more elements had obscured relations and differences which more thorough examination showed to exist (see Tables I. and II.). Consequently there arose a feeling of distrust of much of the older work in the minds of those chemists and petrographers best fitted to judge of its probable qualities. This, and the incompleteness of nearly all the earlier work (and much of that of to-day unfortunately), as shown by the largely increased list of those elements now known to enter into the normal composition of rocks, is rendering the old material less and less available to meet the increasing demands of the petrographer.

And yet these demands on his part are, with few exceptions, by no means so exacting as they should be. Often the analysis is intrusted to the hands of a student without other experience than that gained by the analysis of two or three artificial salts and as many comparatively simple natural minerals, and with a laboratory instructor as adviser whose experience in rock analysis may be little superior to his own. In other words, one of the most difficult tasks in practical analysis is expected to be solved by a tyro, and his results are complacently accepted and published broadcast without question. Even to those thoroughly familiar with the subject rock analysis is a complex and often trying problem. Although long practice may have enabled one to do certain parts of it almost mechanically, one is still from time to time confronted with perplexing questions which require trained judgment to properly meet and answer, and there is still room for important work in some of the supposedly simplest quantitative determinations. If the results are to have any decided value for purposes of scientific interpretation and comparison, they should be the product of one competent to find his way through the intricacies of an analysis in which from fifteen to twenty-five different components are to be separated and estimated with close approach to accuracy, and this a beginner cannot hope to do in the majority of cases. The conscientious chemist should have a live interest in this matter. He should work with a twofold purpose in view—that of lightening the labours of those who come after him by enabling them to use his work with less supplementary examination, and of thereby enhancing his own reputation by meriting encomiums on work that has stood the test of time.

The petrographer, again, should seek to have his analyses made as complete as possible, and not, as is so often the case, be content with determinations of silica, alumina, the oxides of iron, lime, magnesia, the alkalis, and water. The latter, it is true, are entirely justifiable at times, and may serve the immediate purpose for which they were intended, but their incompleteness may, on the other hand, not only conceal points fruitful

* The same thing has been found to hold true in the case of other enzymes. See Vines, *Ann. of Bot.*, 1891, 409; Wortmann, *Bot. Zeit.*, 1890, 37 *et seq.*; Brown and Morris, *Journ. Chem. Soc. Trans.*, 1893, 604.

† *Bulletin of the United States Geological Survey*, No. 176.

of suggestion to the attentive mind, but, what is of still greater importance, they may be actually misleading. Enough instances of totally inaccurate conclusions to be drawn from them have fallen under my own observation to fully justify this plea in favour of greater completeness in rock and mineral analyses made for purely scientific purposes.

The importance of the points indicated in the foregoing paragraph is shown by the difference between the analyses given in Table I. The specimens were taken and analysed at widely separated times and by different persons, it is true, but they were unquestionably from the same rock mass, in which, however much the relative proportions of the different mineral constituents might vary within certain limits, there can be no reason to doubt the general distribution of all the elements shown by the second analysis.

TABLE I.

	Earlier analysis.	Later analysis (*a*).
SiO_2	54·42	53·70
TiO_2	—	1·92
Al_2O_3	13·37	11·16
Cr_2O_3	—	0·04
Fe_2O_3	0·61 (*b*)	3·10
FeO	3·52 (*b*)	1·21
MnO	—	0·04
CaO	4·38	3·46
SrO	—	0·19
BaO	—	0·62
MgO	6·37	6·44
K_2O	10·73	11·16
Na_2O	1·60	1·67
Li_2O	Trace	Trace
H_2O below 110° C.	—	0·80
H_2O above 110° C.	2·76 (*c*)	2·61
CO_2	1·82	—
P_2O_5	—	1·75
SO_3	—	0·06
F	—	0·44
Cl	—	0·03
	99·58	100·40
Less O for F ..	—	0·19
		100·21

(*a*). A still more recent analysis of another of the series of rocks of which this is an example has shown that this "later analysis" is itself probably incomplete and incorrect in part—incomplete because of the probable presence of 0·2 per cent or more of ZrO_2, incorrect because of the error in Al_2O_3 resulting from having counted the ZrO_2 as Al_2O_3, and from the fact that titanium is not fully precipitable in presence of zirconium by Gooch's method (the one employed). This latter error involves both the TiO_2 and the Al_2O_3. (See *prox.*, "Gooch's Method").

(*b*). From the fact that repeated determinations of the iron oxides in this and related rocks from the same region show always a great preponderance of ferric oxide, it is not improbable that the figures given for the two oxides in the first analysis were accidentally transposed.

(*c*). In the published analysis it does not appear whether this is total water or, as seems probable, only that remaining above 100° C.

Another instance of similar kind is given (Table II.). Here, again, certain differences are explainable by natural variations in the proportions of the constituent minerals, but it can hardly be doubted that TiO_2, BaO, SrO, P_2O_5, and SO_3 were present in both specimens in approximately the same amounts. In the earlier analysis determinations of some supposed unimportant constituents were purposely omitted, or made only qualitatively, with results that cannot be otherwise than fatal to a full comprehension of the mineralogical nature of the rock.

TABLE II.

	Earlier analysis.	Later analysis.
SiO_2	44·31	44·65
TiO_2	Not estimated	0·95
Al_2O_3	17·20	13·87
Fe_2O_3	4·64	6·06
FeO	3·73	2·94
MnO	0·10	0·17
CaO	10·40	9·57
SrO	—	0·37 (*a*)
BaO	—	0·76
MgO	6·57	5·15
K_2O	3·64	4·49
Na_2O	4·45	5·67
Li_2O	—	Trace
H_2O below 110° C.	0·77	0·95
H_2O above 110° C.	—	2·10
H_2O by ignition ..	3·30	—
CO_2	—	0·11
P_2O_5	—	1·50
Cl	—	Trace
SO_3	—	0·61
	99·11	99·92

(*a*). Not entirely free from CaO.

Prof. F. W. Clarke has shown that the combined percentages of titanic and phosphoric oxides in rocks of the earth's crust, averaged from hundreds of analyses, is 0·8 per cent. When the determination of these is neglected, the error falls upon the alumina. If the latter is then used as a basis for calculating the felspars, it is easy to see that a very large average error in the latter may result, amounting to several per cent of the rock.

In order to more strongly emphasise the importance of completeness in analysis, a few facts brought out by the hundreds of rock analyses made in this laboratory may be cited. It has been demonstrated most conclusively that barium and strontium are almost never-failing constituents of the igneous rocks of the United States and of many of their derivatives. These amounts are usually below 0·1 per cent for each of the oxides of those metals, but higher amounts are by no means uncommon. Furthermore, the weight of barium is almost without exception in excess of that of strontium. But a still more important point is that the igneous rocks of the Rocky Mountain region, so far as examined, show far higher average percentages of both metals than the rocks from the eastern and the more western portions of the United States. The following examples serve to illustrate certain types of Rocky Mountain igneous rocks:—Of seven rocks forming a Colorado series, six held from 0·13 to 0·18 per cent of BaO, while in the seventh the percentage was 0·43. The SrO ranged from 0·07 to 0·13 per cent for six, and was 0·28 for that one highest in BaO. Of thirteen geologically related rocks from Montana, embracing basic as well as acid and intermediate types, the range of BaO was from 0·19 to 0·37 per cent, with an average of 0·30 per cent. Three others of the same series contained 0·10 per cent or less, while the seventeenth carried 0·76 per cent BaO. The SrO ranged from 0·37 per cent in the last instance to an average of 0·06 for the other sixteen. Certain peculiar rocks from Wyoming carry from 0·62 to 1·25 per cent BaO, and from 0·02 to 0·33 per cent SrO. Surely this concentration of certain chemical elements in certain geographic zones has a significance which future geologists will be able to interpret if those of to-day are not.

Again, vanadium is an element which few chemists have ever thought of looking for in igneous rocks, though it has long been known to occur in magnetites and other iron ores. Hayes, in 1875, reported its occurrence in a great variety of rocks and ores. Quoting from Thorpe's "Dictionary of Chemistry":—"It is said to be diffused

with titanium through all primitive granite rocks (Dieulafait), and has been found by Deville in bauxite, rutile, and many other minerals, and by Bechi and others in the ashes of plants and in argillaceous limestones, schists, and sands." It is further reported to comprise, as the pentoxide, up to 0·1 per cent of many French and Australian clays, 0·02—0·03 per cent of some basalts, 0·24 per cent of a coal of unknown origin, and 0·45 per cent of one from Peru. Still later examinations in this laboratory of about 100 rocks, chiefly igneous, covering the whole territory of the United States, show not only its general qualitative and quantitative distribution, but that it predominates in the less siliceous igneous rocks, and is absent, or nearly so, in those high in silica. In some of the more basic rocks, it occurs in sufficient amount to seriously affect the figures for the oxides of iron unless separately estimated and allowed for (see *prox.*, "Vanadium")—a matter of considerable importance, since the petrographer lays great stress on accuracy in their determinations.

This same investigation has also thrown some light on the distribution of molybdenum, which seems to be confined to the more siliceous rocks, and to occur in quantities far below those commonly found for vanadium.

Finally, had it not been the writer's practice of late years to look for sulphur in rocks, even when no sulphides were visible to the eye, its almost invariable presence in the form of sulphide, and consequent connection with the long mystifying lack of agreement between results for ferrous iron obtained by the Mitscherlich and the hydrofluoric acid methods, might not have been suspected. (See *prox.*, "Ferrous Iron").

While strongly upholding the necessity for more thorough work, necessarily somewhat at the expense of quantity, it is far from the writer's intention to demand that an amount of time altogether disproportionate to the immediate objects to be sought should be expended on every analysis. But it is maintained that, in general, the constituents which are likely to be present in sufficient amount to admit of determination in the weight of sample usually taken for analysis—say, 1 grm. for SiO_2, Al_2O_3, &c., to 2 grms. for certain other constituents—should be sought for, qualitatively at least, in the ordinary course of quantitative work, and their presence or absence noted among the results. If present in little more than traces, that knowledge alone may suffice, for it is often more important to know whether or not an element is present than to be able to say that it is there in amount of exactly 0·02 or 0·06 per cent. In the tabulation of analyses a special note should be made in case of intentional or accidental neglect to look for substances which it is known are likely to be present. Failure to do this may subject the analyst to unfavourable criticism, when at some future time his work is reviewed and the omissions are discovered by new analyses.

Finally, whenever possible, a thorough microscopical examination of the rock in thin section should precede the chemical analysis. This may be of the greatest aid to the chemist in indicating the presence of unusual constituents, or of more than customary amounts of certain constituents, whereby, possibly, necessary modifications in the analytical procedure may be employed without waste of time or labour.

(*Note.*—The foregoing tables and accompanying remarks, including several sentences preceding the tables, have been largely taken from the writer's papers entitled "A Plea for Greater Completeness in Chemical Rock Analysis," published in the *Journal of the American Chemical Society*, 1894, vol. xvi., pp. 90—93; also in the Chemical News, 1894, vol lxix., p. 163. See also "Distribution and Quantitative Occurrence of Vanadium and Molybdenum in Rocks of the United States," in the *American Journal of Science*, 1898, 4th Series, vol. vi., p. 209; and Chemical News, 1898, vol. lxxviii., p. 216).

II. *Object and Scope of the Present Treatise.*

The literature relating to analysis of silicates is extensive but scattered, and in no single article is there to be found a satisfactory exposition of the methods to be followed or the precautions to be observed, especially in the search for some of the rarer constituents or those which, without being rare, have been of late years recognised as occurring persistently in small amounts. It is not intended to make this article a treatise on mineral analysis, but it is believed that the experience gained by the chemists of this Survey during the twenty years since the establishment of its first chemical laboratory in Denver may be useful to most chemists interested in mineral and especially rock analysis.

The original publication of these data in *Bulletin* No. 148 was primarily intended to show the principles and methods according to which the major part of the very many hundreds of analyses therein brought together had been executed, and thus to furnish a partial measure of the trustworthiness of those analyses, rather than to serve as a practical manual of rock analysis. But the use which has been made by mineral chemists of that Bulletin has seemed to render it advisable to amplify somewhat in detail and to add, besides a few new methods, a number of alternative ones which are known or believed to be good, in order that those who may wish to use this treatise as a practical guide shall have a choice from which to select in case the rather expensive apparatus or complicated arrangements sometimes preferred are not available. Where silicate analyses are very frequently made, however, it is a saving of time and of money in the end to set up permanent arrangements for convenience in estimating water, carbon dioxide, ferrous iron, making reductions in hydrogen, &c.

Stress will be laid on those points meriting particular attention, and now and then a brief discussion or criticism of methods elsewhere in vogue may be entered into.

In the earlier years of the existence of the Washington laboratory opportunity was afforded for the testing of novel methods and the devising of new ones, with most excellent results, as shown especially by the methods for separation of titanium, of lithium, and of boron, due to Prof. F. A. Gooch, to whose inventive skill chemists owe likewise the perforated filtering crucible and the tubulated platinum crucible arrangement for the estimation of water. Of late years the press of routine work has been such as to more fully fill up the time of the much-reduced chemical force, and as a consequence it has been found impossible to subject to critical trial several separation methods of recent origin, some of which seem to be full of promise, or to follow out certain lines of investigation which have been suggested by the observations made in this laboratory. This, then, must be offered in explanation if, in the following discussion, it may seem to some that any of the methods followed are too conservative. In general, the discussion will be confined strictly to such separations as may be required in the analysis of an igneous, metamorphic, or sedimentary silicate rock of complex mineralogical composition, in which the majority—and possibly all—of the ingredients in the list given below may occur in weighable or readily discoverable quantities:—

SiO_2, TiO_2, ZrO_2, Al_2O_3, Fe_2O_3, Cr_2O_3, V_2O_3, FeO, MnO, NiO, CoO, MgO, CaO, SrO, BaO, ZnO, CuO, K_2O, Na_2O, Li_2O, H_2O, P_2O_5, S (usually as pyrite, not infrequently as pyrrhotite, occasionally as lazurite), SO_3, C (as graphite or coaly matter), CO_2, Fl, Cl, N.

The special problems often arising in the analysis of rocks of extra-terrestrial origin—the more or less stony meteorites—will not be considered. An analysis of that kind should never be entrusted to the novice, but only to the chemist who has a knowledge of the composition and properties of the peculiar mineral constituents of those bodies and a judgment fit to cope with the oftentimes difficult problems presented by them.

Thorium, cerium, and other rare earths are seldom

encountered in quantities sufficient to warrant the expenditure of the time necessary for their isolation. A search for them qualitatively even is at present rarely justifiable, unless there is microscopic or other evidence of the presence of minerals likely to contain them. Tantalum, columbium, boron, and glucinum have never been certainly met with in the writer's experience, and yet they must be present in certain rocks, and doubtless traces have been overlooked at times. There is no reason to suppose that other elements may not be found by careful search, possibly all in the known category, and, indeed, Sandberger's researches have shown to what an extent this is true of a large number of those elements contributing to the filling of metalliferous veins. But those in the above list may usually be estimated with ease in weights of from ½ to 2 grms.

If the point be raised that many of the published analyses emanating from the Survey laboratories, even the earlier ones of the writer, are not in accord with the advocacy of completeness contained in the foregoing remarks, it may be remarked that these ideas have been to a considerable degree evolved during a personal experience of twenty years in this line of work, and that frequently the exigencies were such as to compel restriction in the examination. Where the latter has been the case, subsequent developments have in some cases shown it to be bad policy in every respect. It is better, both for the geologist and the chemist, to turn out a limited amount of thorough work than a great deal of what may prove to be of more than doubtful utility in the end.

III. *Statement of Analyses.*

Until recently it has been the practice in this laboratory to tabulate the constituents of a rock somewhat in the order of their determination, beginning with SiO_2 as the chief constituent, and grouping together all chemically related oxides, as shown, for instance, in Tables I. and II.

From a strictly scientific point of view, a chemical classification founded on a separation into basic and acidic atoms or radicals would be more satisfactory, but until we learn to find out what silicic radicals are present, and in what relative amounts, also how much free silica there may be, it is useless to think of employing the arrangement so valuable in stating water analyses.

Of late petrographers have begun to demand, with considerable reason, an arrangement "which shall bring the essential chemical features—both the percentage figures and the molecular ratios—prominently and compactly before the eye, so that the general chemical character and the relations of the various constituents may be seen at a glance" (H. S. Washington, "The Statement of Rock Analyses," *Amer. Journ. Sci.*, 1900, Series 4, vol. x., p. 61).

In accordance with this demand it is now our practice to follow pretty closely the arrangement proposed by Pirsson, and very recently strongly advocated by Washington (*loc. cit.*), namely:—

SiO_2, Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O, K_2O, H_2O (above 105—110° C.), H_2O (below 105—110° C.), CO_2, TiO_2, ZrO_2, P_2O_5, SO_3, Cl, Fl, S(FeS_2), Cr_2O_3, V_2O_3, NiO, CoO, CuO, MnO, SrO, BaO, Li_2O, C, Nh_3.

By this arrangement the nine constituents which in the great majority of cases determine the character of the rock are placed at the head of the list, thus greatly facilitating the comparison of different analyses similarly arranged, especially when, as Washington recommends, the molecular ratios are calculated for these leading constituents, and placed immediately after the corresponding oxides. The order of the remaining members is determined some what by the following considerations:—CO_2 is placed next after H_2O, since these two are generally a measure of the alteration the rock may have undergone. TiO_2 and ZrO_2 naturally follow CO_2 on chemical grounds, and SO_3 and Cl, being common constituents of the sodalite group, are conveniently placed together.

Fig. 1.—Platinum-tipped Crucible Tongs.
The parts A B, also of heavy platinum, are hollow, to serve as sockets for the cheaper metal of the handles.

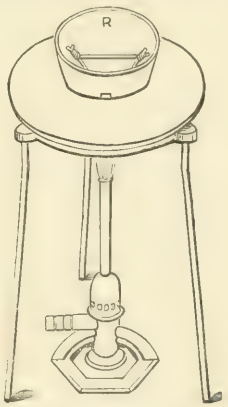

Fig. 2.—Radiator for Rapid and Safe Evaporation.
R is of sheet iron, also nickel (Jannasch). Various sizes. A convenient height is 7 c.m., width at top 7 c.m., and at bottom 5 c.m.

IV. *Time Needed for Making an Analysis.*

The question has often been put, "How long does it take to complete an analysis of this kind?" This will depend, of course, on the mineral complexity of the sample and on the personal factor of the individual worker. If there is a competent assistant to do the grinding, and specific-gravity determinations are not required, it is quite possible after long experience for a quick worker to learn to so economise every moment of time in a working day of seven hours, with an abundance of platinum utensils and continuous use of air and water-baths through the night, as to finish every three days, after the completion of the first analysis, barring accidents and delays, one of a series of rocks of generally similar character, each containing from eighteen to twenty quantitatively determinable constituents, excluding, for instance, fluorine, carbon

as such, nitrogen, metals of the hydrogen sulphide group, and cobalt. On one occasion a series of fourteen rocks, of comparatively simple composition, was completed in one month, with the help of an assistant who made the phosphorus and ferrous iron determinations. But such an output of work is more than exceptional, and implies an unusual freedom from those occasional setbacks to which every chemist is exposed.

It should here be remarked that the Survey laboratory is most exceptionally well equipped with all kinds of platinum vessels and utensils, so that it is rare indeed for delay to arise through lack of dishes of even the largest sizes.

V. *Two Useful Aids in Chemical Manipulation.*

In connection with the foregoing remarks it is in place to mention two aids to the chemist which are in constant use in this laboratory, and have come to be well-nigh indispensable. Neither is novel in principle, and both are in use elsewhere, but they are not so commonly known as they deserve to be, hence this allusion to them.

Fig. 1 represents a form of platinum-tipped crucible tongs devised by Dr. A. A. Blair many years ago. With them a crucible can be securely grasped and brought into any desired position while still hot. To the contents, if in fusion over the blast flame, can be imparted the rotatory motion so often desirable. Above all, the cover need not be in the slightest degree displaced, as when using the common form of platinum-tipped tongs.

Fig. 2 represents a very useful adjunct to the work-table and especially to the draught cupboard, wherein the liquid contents of crucibles can be speedily evaporated at almost any desired temperature, and the dehydration of many solids effected much more safely than on an iron plate or sand-bath. I do not recall who orginated this form of air-bath, but it has been in use here for over fifteen years, and is identical in principle with the later Nickel-becher of Jannasch. Nickel undoubtedly has a certain advantage in not rusting as does iron, but the form depicted in R of Fig. 2 can easily be made anywhere of sheet iron rivetted at the joint, the bottom (not shown in the figure), being securely held by a flange at the extremity of the truncated cone. A crucible placed on the platinum triangle becomes uniformly heated by hot air, and large quantities of liquid, even sulphuric acid, can be thus volatilised in a short time without ebullition or spattering.

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL INSTITUTION ADDRESS TO THE KING.

At the General Monthly Meeting of the Royal Institution held on Monday last, the 4th inst., the following Address to the King was read and approved, and authorised to be signed by His Grace The Duke of Northumberland, K.G., the President, on behalf of the Members:—

To the King's Most Excellent Majesty.

The humble Address of the Members of the Royal Institution of Great Britain.

Most Gracious Sovereign,

We, your Majesty's most loyal and dutiful subjects, the Members of the Royal Institution of Great Britain, established for the promotion of Science, Literature, and the Arts, respectfully crave leave to approach your Sacred Person with expressions of our heartfelt sorrow at the loss sustained by your Majesty, the Royal Family, the Empire, and the World at large, in the death of your Majesty's revered Mother, our late most gracious and beloved Sovereign and Patron of this Institution: and also to testify our unfeigned congratulations upon your Majesty's Accession to the Throne, as well as our sincere attachment to your Royal Person.

That your Majesty may long live in Prosperity and Happiness over a free and affectionate people is the sincere wish and earnest prayer of

Your Majesty's Loyal and Dutiful Subjects,
The Members of the Royal Institution of Great Britain.

The President, in moving a Vote of Condolence on the Death of Her late Majesty, remarked that Her Majesty had been for the whole of Her reign the Patron of this Institution. She had shown her keen appreciation of the value of scientific study and research by the honours she had conferred from time to time on those who followed them. There was one signal act of kindness which should be recorded in connection wth this Institution, namely that she gave to Professor Faraday rooms in Hampton Court Palace, and that when he found himself unable to meet the expense of necessary repairs she took it upon herself. Her Husband and Sons had been frequent attendants at our Lectures, but perhaps the highest debt of gratitude which scientific men owed to our late Sovereign was that she had by her wisdom and skill secured them through a prolonged reign the utmost freedom and tolerance of thought and action, combined with complete order and stability of government, a condition of things most favourable to the pursuit of Science. He was sure that the Members of the Royal Institution shared to the fullest extent the regard which the whole of her people, from the lowest to the highest, had evinced to her memory.

NOTICES OF BOOKS.

Inorganic Chemistry, Non-metallic and Metallic Elements. By Raphael Meldola, F.C.S. Revised to date by J. Castell Evans, F.I.C. Fifth Edition. London: Thomas Murray.

Professor Meldola's Chemistry made its first appearance more than twenty years ago, and it speaks well for the care with which it was originally prepared, that it has been steadily in demand up to the present date, though unrevised till now.

The author's original aim was not to provide the student with a means of cramming, so as to simply get through an examination, but to compress as much thorough, sound chemistry as possible into a small space, making a book that not only would bear, but required to be closely studied.

Owing to the recent rapid advance made in all branches of chemical science, the book naturally fell a little behind the times; the necessary revision has, however, now been taken in hand, and the book has been brought up to date while retaining its characteristic excellence.

The greatest change will be found in the sections devoted to the metallic elements; these have been rearranged in accordance with Mendeleeff's law, and are quite up to the standard of the earlier editions.

Report of the Senior Analyst, Cape of Good Hope, for the Year 1899. Cape Town: W. A. Richards and Sons. 1900.

Although in some respects there has been a falling off in the number of articles analysed, there has been on the whole a considerable increase owing to the work under the Food, Drugs, and Seeds Adulteration Act having been more regularly maintained than in former years. The total number of samples analysed during the year 1899 was 1903, compared with 1650 and 979 in the two previous years. There have been most samples of milk analysed, viz., 481, closely followed by sea-water, 397; then come soils, 161, and water, 142.

With regard to the analysis of sea-water, it is stated that "these analyses have been continued on behalf of the Colonial Marine Biologist. No special remarks need here be made concerning them." It would be interesting to know why such a large number (397) were undertaken, whereas there were only 142 analyses made of ordinary or so-called potable waters. In connection with these latter we may recall the well-known fact that South Africa is a fever-stricken country; this is not to be wondered at when we look over a few of the analyses of waters of which details are given. As an example of the extent to which animal pollution can go we cite the analyses of a well-water at Retreat Police Station:—

Total solids	66·92	grms. per gallon
Chlorine	18·81	„ „
N as Nitrates	0·052	„ „
N as Ammonia	1·202	parts per million
Oxygen absorbed from permanganate in four hours	129·362	„ „
Colour	Dark brownish red	
Appearance	Clear	

This is, of course, an extreme case, but there are numerous other analyses given in which the oxygen absorbed is 11·1, 9·6, 8·1, 7·6, 8·8, &c., parts per million. We are not surprised that such waters as these are condemned as being unfit for human consumption.

The Chemists' Pocket Manual; A Practical Hand-book containing Tables, Formulas, Calculations, Physical and Analytical Methods, for the use of Chemists' Assayers, Metallurgists, Manufacturers, and Students. By G. Richard K. Meade, B.S., Instructor in Chemistry in Layfayette College, Easton, Pa. Easton, Pa.: The Chemical Publishing Company. 1900.

It is a pity that this useful and up to date little manual has not been translated into English, for valuable though it undoubtedly is to American workers it is not likely in its present form to come into great use here. The words sulfur, sulfuric, oxid, hydroxid, and liter look strange, while the ton of 2000 pounds, and the gallon of 231 cubic inches are liable to cause confusion. At the same time there will be found a mass of useful and original data condensed into a small compass; the several examples of graphic methods for saving calculations are very good; examples are given of a table on squared paper for instantly finding the equivalent weights of magnesium pyrophosphate and phosphorus pentoxide, conversion of $Mn_2P_2O_7$ into Mn, $Mg_2P_2O_7$ into MgO, &c. The main object in the book appears to be to "save time." There is a good index, and it is well printed on thin but strong paper, with a flap and band to close it for the pocket.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, del'Académie des Sciences. Vol. cxxxii., No. 2, January 14, 1901.

Researches on the Formation of Organic Compounds containing Sulphur.—M. Berthelot.—During previous researches, the author examined thermo-chemically carbon disulphide, thiophene, taurine, and the isomers of the sulphocyanic compounds, and he now examines certain fundamental bodies, such as the alcohols and simple ethers; this preliminary examination being devoted to the alcohols containing sulphur, otherwise called mercaptans. The heats of formation, of molecular combustion at constant pressure, and formation from the elements, were found in the case of ethylic mercaptan, C_2H_6S; ethyl sulphide, $C_4H_{10}S$; amylic mercaptan, $C_5H_{12}S$; amyl sulphide, $C_{10}H_{22}S$; and allyl sulphide, $C_6H_{10}S$.

New Researches on the Isomerism of Sulphocyanic Ethers.—M. Berthelot.—It is known that two isomeric series of sulphocyanic ethers exist, under the names of normal sulphocyanides and isosulphocyanides; the latter being the more stable. The author proves that this difference of stability is explained by the thermochemical relations, the transformation from normal sulphocyanides into isosulphocyanides being accompanied by evolution of heat (+10·5 cal. for the methylic ethers, and +9·0 cal. for the ethylic ethers). In each case the substance was burnt in the calorimetric bomb; an estimation each time being made of the sulphur transformed into sulphuric acid during the combustion.

Gaseous Products Evolved when certain Igneous Rocks are Heated.—Armand Gautier.—The author's researches on the origin of atmospheric hydrogen and on the constitution of deep-sea water, led him to the examination of rocks, which, at the moment when they were fixed in their actual position, supported an enormous pressure due to superposed layers. He has already noticed that the mineral acids towards 100°, and pure water itself towards 300°, cause the evolution of a considerable proportion of gas rich in hydrogen from powdered granite. This same evolution occurs from all the igneous rocks which were examined. The quantity and the composition of these gases vary from each specimen, and even from different pieces of the same rock. The gases from various rocks were analysed, and the results are given in this paper.

Action of Hydrogen on Bismuth Protosulphide.—H. Pélabon.—The protosulphide of bismuth, BiS, obtained by melting together bismuth and sulphur in proper proportions, is reduced by means of hydrogen if it is heated in a current of this gas. Inversely, melted bismuth decomposes sulphuretted hydrogen gas. If these reactions take place in a space in which every point is at the same temperature, the two reactions lead to a chemical equilibrium. The author examines the two cases:—(1) When the temperature of the experiment is between the fusion-points of bismuth and of its sulphide; (2) when the temperature is above the fusion-point of the sulphide. It is found that the proportion of sulphuretted hydrogen increases very regularly, starting from zero, in the same way as the proportion of bismuth sulphide, and the relation between the mass of sulphuretted hydrogen and the total mass (ρ), tends towards the number 0·893 when the relation between the weight of undecomposed sulphide to the weight of the mixture formed by this body and the bismuth liberated (R) tends towards 1.

Chlorobromides of Thallium of the Type $ThX_3.3ThX$.—V. Thomas.—As a result of the author's researches, he concludes that if the thallium chlorobromides, $Th_4Cl_4Br_2$ and $Th_4Cl_2Br_4$, exist—which is, apparently, doubtful—they are not stable, and decompose during crystallisation, giving $Th_4Cl_3Br_3$. This latter chlorobromide has a very regular form, and is produced when the solution from which it is crystallised is dilute. When, on the contrary, the solution is concentrated and sufficiently rich in thallium compounds, the chlorobromides which are formed are different, and appear to be of the general type ThX_3ThX.

A New Method of Preparation of the Hydrates of Sodium Peroxide and their Properties.—Georges F. Jaubert.—If sodium peroxide is exposed to the action of damp air, free from carbon dioxide, water is absorbed by the peroxide with no evolution of gas. From this it is apparent that hydrates of the peroxide are formed. These probably are $Na_2O_2+2H_2O$ and $Na_2O_2+8H_2O$, besides intermediate hydrates yet unknown. The hydrate $Na_2O_2+8H_2O$ is very stable in the cold, but when heated

to between 30° and 40° it undergoes partial decomposition, and between 80° and 100° the decomposition is total.

Determination of Latent Heats of Vaporisation of certain Organic Compounds.—W. Louguinine.—The author determines the quantities of heat evolved in the calorimeter during condensation of the vapour of the following substances, and from the numbers obtained calculates the latent heat of vaporisation:—Aniline, 104·17; methylethylacetoxime, 115·73; anisol, 80·30; and butyronitrile, 115·25.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 4th inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Mr. J. Boldero, Mr. J. Y. Buchanan, Mr. A. Lyttleton, Mr. J. Macfadyen, Mr. A. W. Reed, Major J. M. Rogers, Mr. D. Weston, and Dr. T. T. Whipham, were elected Members. The special thanks of the Members were returned to Sir Frederick Abel, Bart., K.C.B., for his donation of £50, and to Professor Dewar for his donation of £50, to the Fund for the Promotion of Experimental Research at Low Temperatures. The following Resolution, passed by the Managers, was read:—"Resolved, That the Managers of the Royal Institution desire to record their sense of the loss sustained by the Institution in the decease of Mr. Basil Woodd Smith, F.R.A.S., F.S.A. He became a Member of the Royal Institution in 1853, and was elected a Visitor in 1876, and a Manager in 1889. He has always taken a warm interest in the welfare of the Institution, and for many years as Manager and Vice-President he rendered valuable assistance in the transaction of the business affairs and concerns of the Institution. The Managers further desire to offer to the Family the expression of the most sincere sympathy with them in their bereavement."

Note on the Action of Sulphuretted Hydrogen on Peroxide of Lead.—L. Vanino and O. Hauser.—When we pass SH_2 over peroxide of lead, either dry or moist, the mass becomes incandescent, and the sulphuretted hydrogen burns with the livid blue flame of lead; peroxide of bismuth gives rise to the same occurrence. Hilger, Silge, and van Scherpenberg have already mentioned this phenomenon, but they only observed it with the dried reagents. This reaction may be utilised for communicating fire to explosive mixtures. Thus, gun-cotton completely saturated with water, can be ignited by means of sulphuretted hydrogen and peroxide of lead. Picrate powder, the metallic aluminium, zinc, and bismuth powders can also be ignited by this means; to ensure the reaction taking place it is necessary for the binoxide of lead to be collected together in a mass, and not spread over a surface.—*Berichte*, vol. xxxiii., p. 625.

MEETINGS FOR THE WEEK.

Monday, 11th.—Society of Arts, 8. (Cantor Lectures). "The Bearings of Geometry on the Chemistry of Fermentation," by W. J. Pope.

—— Royal Institution, 3. "The Origin of Vertebrate Animals," by Arthur Willey, M.A., D.Sc.

Tuesday, 12th.—Royal Institution, 3. "Practical Mechanics" (Experimentally treated), by Prof. J. A. Ewing, M.A., F.R.S., M.Inst.C.E.

—— Society of Arts, 8. "Recent Advances in Pottery Decoration," by William Burton.

Wednesday, 13th.—Society of Arts, 8. "Arsenic in Beer and Food," by William Thomson, F.I.C.

Thursday, 14th.—Society of Arts, 4.30 (at the Imperial Institute, South Kensington). "The Greek Retreat from India," by Col. Sir T. Hungerford Holdich, R.E., K.C.I.E., C.B.

—— Royal Institution, 3. "Society in France before the Revolution," by the Rev. Henry Grey Graham.

Friday, 15th.—Royal Institution, 9. "Electric Waves," by The Rt. Rev. Monsignor Gerald Molloy, D.D., D.Sc.

Saturday, 16th.—Royal Institution, 3. "Vocal Music, its Growth and Decay," by F. Corder, F.R.A.M.

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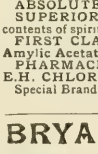

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THE CHEMICAL NEWS.

Vol. LXXXIII., No. 2151.

ON THE PROTEID REACTION OF ADAMKIEWICZ, WITH CONTRIBUTIONS TO THE CHEMISTRY OF GLYOXYLIC ACID.*

By F. GOWLAND HOPKINS, M.A., M.B., University Lecturer in Chemical Physiology, and SYDNEY W. COLE, B.A., Trinity College.

In 1874 Adamkiewicz (*Pflüger's Archiv.*, 1874, vol. ix., p. 156), described the now familiar reaction which results in the production of a violet colour when strong sulphuric acid is added to the solution of a proteid in glacial acetic acid. Adamkiewicz did not apparently look upon the employment of the acetic acid as introducing anything beyond a certain modification of the action of sulphuric acid. His original communication opens with a description of the colour phenomena seen when egg-white is dissolved in strong sulphuric acid; and he begins the description of this reaction, since associated with his name, by speaking of "a special influence which the presence of glacial acetic acid has upon the colour of the sulphuric acid proteid solution." The view has since been generally held that the coloured product of the reaction arises entirely from the proteid molecule itself, as the result of an interaction between precursors liberated under the influence of the strong acids employed.

V. Udranszky (*Zeitsch. f. Physiol. Chem*, 1888, vol. xii., p. 395), believed that the colour change which occurs is, as a matter of fact, to be classed as a furfurol reaction. It is therefore to be compared with the result of such a procedure as that of Molisch's test, in which β-naphthol and sulphuric acid are added to a proteid solution. While in the latter the added naphthol is held to react with furfurol from the proteid; in the Adamkiewicz reaction both the furfurol and a substance capable of reacting with it are supposed to be liberated from the proteid molecule. Such we believe is the prevalent view. Of late years, the Adamkiewicz reaction has been much employed as giving evidence for the presence of carbohydrate groups in certain proteid derivatives, and of its absence from others. More than one writer (*Cf.* Halliburton, "Schäfer's Text Book of Physiology," vol. i., p. 47), however, has referred to an element of uncertainty in the reaction, and it is easy to gather from the literature that this has been commonly observed (*Cf.* Salkowski, *Zeitsch. f. Physiol. Chem.*, vol. xii., pp. 220, 222).

In what follows it will be shown that the mechanism of the reaction has been wholly misunderstood. Proof will be given that the use of acetic acid introduces an extraneous and perfectly specific factor into the reaction, involving the addition of a substance quite necessary to the formation of the coloured product. This substance, moreover, is not acetic acid itself, but an impurity, which, though very generally present, is admixed in varying quantity, and is occasionally absent.

I. *The Reaction due to an Impurity in Acetic Acid.*

We were led to pursue the following investigation by observing that, with a specimen of acetic acid in use in this laboratory last year, it was impossible under any circumstances to obtain the Adamkiewicz reaction.

No matter what form of proteid might be employed, when its solution in this acetic acid was mixed with sulphuric acid, a yellow or brown, slightly fluorescent mixture was all that could be obtained. No modification in the order of the procedure, or in the proportion of the two acids employed, resulted in the production of any trace of red or violet colour.

We afterwards obtained a number of specimens of acetic acid from various makers, and were surprised to find that no small proportion of these gave equally negative results; while, of the remainder, some yielded a much more intense reaction than others, although employed under precisely similar conditions.

Either, therefore, the negative result with particular specimens was due to the presence of some impurity capable of interfering with the production of colour, or the reaction itself must be due to a substance commonly, though not universally, present as an impurity in acetic acid.

We soon obtained evidence that the latter alternative must be accepted. For we found that whenever a specimen of glacial acetic acid yielding a positive result is partially crystallised by freezing, the power to yield the reaction is diminished in the crystals and increased in the mother liquor. It is possible indeed, by repeated recrystallisation, to obtain glacial acid wholly incapable of giving the reaction.

Much more readily, however, is the reactive substance to be concentrated by distillation. Any specimen of glacial acetic acid, if distilled, will yield the whole of any chromogenic substance it may contain in the first runnings. After concentration to about half-bulk—more or less according to the proportion of reactive substance originally present—the residue will yield no trace of red or violet colour when mixed with proteid and sulphuric acid; while, on the other hand, the distillate twice or thrice fractionated yields the reaction with greatly increased intensity.*

It is easy to understand therefore why different specimens of acetic acid obtained in the market yield the reaction with different degrees of intensity, as this will depend upon the stage at which they were collected during distillation in bulk. It is also clear why the reaction has been looked upon by different observers as an uncertain one.

The accepted view, that the colour phenomenon is due to the interaction of two chromogenic groups, both derived from the proteid molecule under the action of the mixed sulphuric and acetic acids, is certainly erroneous. One factor necessary to the reaction is supplied by a substance admixed with the acetic acid. That it is in no sense a furfurol reaction is indicated by the fact that the addition of furfurol confers no power of yielding the colour with proteid upon a specimen of acetic acid previously without it; and, on the other hand, when furfurol is added to acetic acid containing the chromogenic substance in abundance, there is equally a complete absence of the reaction upon mixing with strong sulphuric acid.

II. *Nature of the Substance responsible for the Reaction.*

Our earlier attempts actually to isolate the active substance from acetic acid by fractional distillation were unsuccessful; and, having regard to the fact that, in a reagent so familar as acetic acid, no admixture could well have been hitherto overlooked unless the substances were present in very small amount, we determined to seek first for indirect evidence, such as might give at least some indication as to the kind of substance we had to deal with.

To this end we set out to add to acetic acid, previously deprived by distillation of its chromogenic admixture, various compounds of typical constitution, in the hope that we might find among these some that would yield at least an analogous reaction.

Wholly negative results were obtained with various homologous fatty acids; with formic, acetic, and propionic

* From the Physiological Laboratories, Cambridge. A Paper read before the Royal Society, February 7, 1901.

* This applies to glacial acid; with dilute acid of lower boiling-point, concentration of the product by distillation is less easy.

aldehydes; with acetone, and with various ethereal acetates and other esters.

But, during this preliminary stage of our investigation, the interesting observation was made that formic acid prepared from pure glycerin and pure oxalic acid, and used instead of acetic acid under the ordinary conditions necessary for the reaction, may yield the colour in a perfectly typical manner; the spectroscopic absorption of the product obtained being identical with that seen when acetic acid is used. But from the formic no less than from acetic acid, the chromogenic substance may be distilled off, appearing always in the earlier portions of the distillates, and leaving the remainder of the formic acid to yield wholly negative results.

This result—the explanation of which becomes clear in the sequel—appeared to limit somewhat the ground we had to traverse in our search.

A further and still more definite limitation came to light when we found that the reactive substance in acetic acid is not an impurity of wholly extraneous origin, but is a derivative of acetic acid itself. When a quantity of acetic acid wholly free from the reactive substance has stood for a few weeks, a reaction may always be obtained once more from the earliest portions of a distillate; and, after standing for a month or two, even the bulk may yield a colour of moderate intensity. (*Cf. infra*).

When, again, a pure acetate, and especially calcium acetate, is distilled with excess of sulphuric acid, the first runnings always give a marked Adamkiewicz reaction, though later portions give none. This is true even when the acetate has been made by neutralising acid which was itself wholly incapable of giving a reaction.

Lastly, among the products of the dry distillation of most acetates small quantities of a substance are found which react with proteid in a typical manner. In the case of calcium acetate the reaction obtainable is a marked one—though, as stated above, the active substance is certainly not acetone—while with an aqueous extract of the products of the dry decomposition of mercuric (not mercurous) acetate the reaction with proteid is intense.

With such indications as these facts afforded, we now fortunately elected to experiment with various two-carbon compounds of typical structure, such as might conceivably arise from acetic acid, by oxidation or otherwise.

The first positive evidence came to light when we set out to prepare glycollic aldehyde by Fenton's method (*Journ. Chem. Soc.*, 1895, vol. lxvii., p. 778). As a mere preliminary observation, we oxidised tartaric acid in solution, by means of peroxide of hydrogen in the presence of a little ferrous sulphate, without taking especial care to keep the mixture at 0°, and without attempting to separate the dioxymaleic acid formed. A little of the oxidised solution was heated direct on the water-bath till all evolution of CO_2 had ceased, and then cooled. A trace of Witte's peptone was added to the solution, which was free from excess of peroxide, and then strong sulphuric acid. An intense colour reaction was obtained exactly similar to that seen in a normal Adamkiewicz reaction when carried out with acetic acid rich in the chromogenic substance. The solution gave also in the spectroscope an exactly similar absorption band.

We found subsequently, however, that glycollic aldehyde, isolated, either in the syrupy or crystalline condition,* and whether in aqueous or acetic acid solution, gave no colour reaction under like conditions, but yielded only a charred product when the sulphuric acid was added. Moreover, acetic acid, however rich in the chromogenic substance, never reduces (after neutralising) alkaline copper solutions. A reduction of ammoniacal silver solutions may be obtained, but never any effect upon Fehling's solution.

We came to the conclusion therefore that the substance sought must be an oxidation product of glycollic aldehyde; and we now found that the latter needs only to be treated by Fenton's oxidation method carried out at the temperature of the water-bath to give a product, which, when free from excess of peroxide, yields in acetic or aqueous solution the proteid reaction abundantly.

At this time we made another observation of the greatest assistance to our inquiry, finding that the chromogenic substance is produced in abundance when oxalic acid is reduced in aqueous solution by means of zinc and sulphuric acid, or, more conveniently, by sodium amalgam.

The reduction need last for a few minutes only, and a little of the solution, without further treatment, will then be found to give an intense colour with proteid and sulphuric acid, the product showing spectroscopic appearances identical with those of the ordinary Adamkiewicz reaction.

There was now no doubt that a colour reaction, not to be distinguished from that of Adamkiewicz, is yielded by a substance which is at once an oxidation product of glycollic aldehyde, and a reduction product of oxalic acid. It was difficult to see how this substance could be other than glycollic acid, glyoxylic acid, or glyoxal.

Pure glycollic acid was obtained from Merck. It gave no trace of a colour reaction with proteid solution and sulphuric acid. The product of its oxidation by Fenton's method reacted, however, in a perfectly typical manner, and Fenton and Jones have found that this product is glyoxylic acid.

The latter was therefore prepared from alcohol by the method of Debus. The calcium glyoxylate first obtained was re-crystallised thrice. A minute crystal of the salt dissolved in water, together with a little proteid, gave, upon the addition of strong sulphuric acid, a vivid colour reaction not to be distinguished, spectroscopically or otherwise, from the reaction of Adamkiewicz.

Glyoxal, prepared subsequently from the products of the same Debus oxidation, gave no trace of such a reaction.* When glyoxylic acid is added to glacial acetic acid previously deprived of its chromogenic power by distillation, further distillation now yields a distillate which reacts typically, and the glyoxylic acid comes over characteristically, like the original chromogenic substance in the earlier fractions.

III. *Glyoxylic Acid from Acetic Acid.*

It now became necessary to ascertain whether glyoxylic acid is, as a matter of fact, present in such specimens of acetic acid as yield the Adamkiewicz reaction.

In seeking for evidence as to this, it was necessary to remember that exceedingly little glyoxylic acid is necessary to the reaction. With an aqueous solution of such strength as will give no more than an opalescence with phenylhydrazine, the colour reaction with proteid is well marked.

It was found, however, that oxidation with hydrogen peroxide confers abundant chromogenic power upon acetic acid previously giving no proteid reaction: and it was our first endeavour to ascertain whether, as a result of this, glyoxylic acid is produced in quantity sufficient for its easier identification.

The presence of small quantities of ferrous iron accelerates the oxidation, and is, perhaps, essential to it.† The process occurs most rapidly at boiling temperature, and proceeds most satisfactorily when the acetic acid is repeatedly distilled with the peroxide. The limit of the oxidation is in any case soon reached. Using twenty

* Fenton and Jackson, *Journ. Chem. Soc.*, 1899, vol. lxxv., p. 575. We were indebted to Mr. Hy. Jackson for a supply of the crystalline aldehyde.

* Many specimens of commercial glyoxal give the reaction, but only, as we have found, when they contain glyoxylic acid; preparations of glycollic acid may contain traces of the latter.

† We have found that some specimens of peroxide bring about the oxidation without the addition of iron; others undoubtedly act much less readily, unless a ferrous salt is added. While we have been unable to detect the presence of iron in the former, so small a quantity appears to affect the reaction that it is possible a trace of the metal present as an impurity may account for the difference.

volumes strength, the peroxide is found to be rapidly destroyed till a volume has been added about equal to that of the acetic acid taken; after this the reaction becomes very slow.

We proceeded as follows:—A litre of glacial acetic acid was mixed with an equal bulk of twenty-volume peroxide and some ammonio-ferrous sulphate added (half a grm. per litre, or less). The mixture was slowly distilled nearly to dryness, and the distillate returned and again distilled. The second or third distillate usually showed freedom from peroxide when tested with chromic acid; if not, distillation was repeated.

One-tenth of the final distillate was set aside, and the remainder neutralised with potash. The still acid portion being then mixed with the rest, the whole was distilled as low as possible, avoiding, however, any separation of potassium acetate in the retort. The distillate always gave an abundant proteid reaction, and if any trace of free peroxide had been left at the previous stage, it always disappeared during the distillation of the partially-neutralised mixture as just described. A small trace of free peroxide will interfere with the proteid reaction. On adding phenyl hydrazine hydrochloride (without acetate) to the distillate thus obtained, a light yellow precipitate begins to separate almost at once, and after standing it becomes considerable in amount, and is crystalline. But although, as we were able to show, the hydrazone of glyoxylic acid is present in this precipitate, it is mixed with a considerable proportion of a compound much less soluble in acetic ether and in hot water. If the original precipitate be re-crystallised from a minimal quantity of acetic ether, the substance which separates first consists of perfectly colourless glistening plates, which after re-crystallising from acetic ether may assume the form of rosetted prismatic needles. These melt sharply at 184°.

The nature of this substance became clear after the publication of certain recent observations. Gerhard Ollendorff has shown that formic aldehyde is formed when glycollic acid is oxidised with peroxide of hydrogen, and Fenton (*Journ. Chem. Soc.*, 1900, vol. lxxvii., p. 1296), calls attention to the fact that glyoxylic acid must in this case be the intermediate product. The product we obtained from acetic acid was undoubtedly the compound of formaldehyde described by Wellington and Tollens (*Deutsch. Chem. Ges. Berichte*, 1885, vol. xviii., p. 3330).

A portion repeatedly re-crystallised from acetic ether and showing a constant melting point (184°) was analysed.

0·147 grm. gave 27·4 c.c. moist N at 12° and 758 m.m. N = 22·07 per cent.

Another preparation, re-crystallised from a mixture of alcohol and toluol, melted at 182—183°; of this—

0·211 grm. gave 39·3 c.c. moist N at 14° and 758 m.m. N = 21·87 per cent.

I.	II.	Calculated for $C_{18}H_{16}N_4$.
22·07	21·87	22·22

This hydrazone can be obtained pure in the above manner with great ease if not more than 4 to 5 grms. of phenylhydrazine hydrochloride have been added to the final distillate obtained after oxidising, as above, 1 litre of acetic acid, nearly neutralising the mixture, and distilling. We prepared the compound from formaldehyde, and found it to agree with our product in every particular.

Formaldehyde certainly does not yield the proteid reaction, and its formation when acetic acid is treated as described seems to be in itself evidence for the formation of glyoxylic acid during the process, as it is difficult to see how it could arise during the oxidation of acetic acid if not from a preliminary formation of glyoxylic acid with subsequent loss of carbon dioxide.

But its formation adds greatly to the difficulty of obtaining pure the hydrazone of glyoxylic acid itself, especially as the precipitate produced by phenylhydrazine undoubtedly contains, in addition to the compound of Wellington and Tollens, smaller amounts of the derivatives described by J. W. Walker (*Journ. Chem. Soc.*, 1896, vol. lxix., p. 1280).

After the nature of this by-product was recognised we modified our procedure by neglecting the earlier portions of the final distillate which contains, of course, the greater part of the formaldehyde. Phenylhydrazine hydrochloride added to the latter half, or two-thirds, of such a distillate yields a precipitate which forms more slowly than that obtained when the whole is dealt with. After twenty-four hours it is usually crystalline and of a yellow colour, growing darker with further standing.

We found it easier to obtain a product with a constant melting point by re-crystallising from hot water rather than from an organic solvent, prolonged heating with the water being at any stage avoided. This treatment involves considerable loss, however, and we obtained only about 4 decigrms. of the hydrazone after oxidising 3 litres of acetic acid. This, however, had all the characters of glyoxylic hydrazone, and melted sharply at 137°.

0·204 grm. gave 30·4 c.c. moist N at 16° and 750 m.m. N = 17·14 per cent. Calculated for $C_8H_8O_2N_2$ = 17·07.

When acetic acid has been oxidised as described and the mixture partially neutralised and distilled, the distillate, when treated with excess of chalk, will yield, after standing and filtering, the reaction for glyoxylic acid described by Perkin and Duppa. If after treatment with chalk a slight excess of calcium hydrate be added, and the mixture concentrated *in vacuo* to about one-third its original bulk, this reaction with aniline oxalate is obtained in a highly characteristic manner.

The methods we have hitherto employed do not yield the glyoxylic acid in solutions of sufficient strength to permit of its calcium salt being separated from the associated acetate and isolated in substance. The ease with which the salt dissociates and the volatility of the acid with water vapour make concentration of small avail.

The evidence for the formation of glyoxylic acid during oxidation appears, however, to be conclusive, and it is interesting to note that, judging from the gradual development of the reaction with proteid, this oxidation goes on slowly when acetic acid is exposed to air, and especially under the influence of light. Ferrous iron undoubtedly accelerates this, and if acetic acid giving no proteid reaction be somewhat diluted, and a little ferrous salt added, exposure to direct sunlight will confer a reactive power in the course of a few hours.

We have not been able to separate the hydrazone in quantity sufficient for its identification from average specimens of untreated acetic acid; but it appears equally difficult to do so when small quantities of glyoxylic acid, sufficient to confer an average chromogenic power, have been added to a specimen previously giving no reaction.

On one occasion we obtained a quantity of glacial acid giving the reaction with special intensity. This acid had crystallised in bulk, and we were supplied with drainings from the crystals. Seven litres were fractionally distilled until the chromogenic substance was concentrated into about 1 litre. This was nearly neutralised and again distilled. Phenylhydrazine acetate added to the distillate gave a considerable quantity of crystalline precipitate, yellow at first, darkening on standing. This was obtained before we had identified glyoxylic acid as the substance sought, and most of the hydrazone was lost in preliminary solubility tests. A small quantity was reserved, however, and this, re-crystallised thrice from hot water, melted sharply at 137°.

The observations we have hitherto made give no quantitative indications of any value. In this paper we have been mainly concerned with the endeavour to prove the nature of the active substance in the proteid reaction. We propose to study the oxidation of acetic acid further, and to define if possible the conditions necessary for a maximal yield of glyoxylic acid.

(To be continued).

THE DETECTION AND ESTIMATION OF MINUTE QUANTITIES OF MANGANESE.

By HUGH MARSHALL, D.Sc.

THE most delicate test for manganese in solution consists in converting it into permanganate, recognisable by the colour it imparts to the solution. At present this is generally effected in the way first proposed by Walter Crum—oxidation by means of lead peroxide in presence of nitric acid. The excess of peroxide must be allowed to settle before the colour can be observed, and the presence of the former interferes with the delicacy of the reaction when minute traces of manganese are concerned. It is evident that the test would be greatly improved by the use of an oxidising agent which was itself colourless and soluble.

When a manganese salt is heated with a solution of persulphate the manganese is precipitated as peroxide, precipitation being complete under suitable conditions; by digestion of the mixture for some time a pink solution is sometimes obtained, a small quantity of permanganate apparently being formed, but the production of the pink colour cannot be effected with certainty. Recently, I discovered that the presence of a trace of a silver salt has a remarkable effect on persulphate solutions, greatly accelerating their oxidising action, and apparently, in some cases, bringing about oxidations which would not otherwise occur. Thus, ammonium persulphate solution, to which a small quantity of silver nitrate has been added, undergoes decomposition in the manner indicated by the equation—

$$4(NH_4)_2S_2O_8+3H_2O=7NH_4HSO_4+H_2SO_4+HNO_3.$$

Such actions seem to depend on the formation and decomposition of silver peroxide, which is probably produced by action of water on silver persulphate—

$$Ag_2S_2O_8+2H_2O=2H_2SO_4+Ag_2O_2.$$

This method of oxidation appeared as if it might be suitable for the conversion of manganous salt into permanganate, and experiments confirmed this view. Minute quantities of manganese could be quite easily detected by gently warming the solution with persulphate, in presence of sulphuric or nitric acid, and with addition of a drop of dilute silver nitrate solution. With small quantities there is no separation of manganese peroxide; the solution remains quite clear, but rapidly assumes the characteristic pink colour when a suitable temperature has been reached.

In order to determine the delicacy of the reaction a standard solution was prepared by dissolving 0·029 grm. of potassium permanganate in a litre of water. Some of this was kept for comparison, and the remainder was reduced by the addition of a drop or two of sulphurous acid; the latter then contained one hundredth of a milligrm. of manganese, as manganous salt, per c.c. 1 c.c. of the solution was run into a test-tube containing a pinch of re-crystallised potassium persulphate; a drop of sulphuric acid and a drop of dilute silver nitrate solution were then added, and the mixture was warmed. An unmistakable pink colour was produced. It was found that a distinct colouration could still be obtained when only two drops of the solution (about 0·1 c.c., containing one thousandth of a milligrm. of manganese) were employed, the total quantity of liquid being about half a c.c. This seems to be approximately the limit to which the test is applicable.

In carrying out the test only a minute quantity of silver salt should be employed, otherwise there may be separation of finely divided silver peroxide; it is not advisable to boil the liquid, but rather to allow it to stand for a little at a moderate temperature; while the liquid should be acid, it should be only moderately so, as the reaction does not take place in presence of very concentrated sulphuric or nitric acid; only a small quantity of persulphate is necessary, and either the potassium or the ammonium salt may be employed. Potassium persulphate is much more easily purified than the ammonium salt, and keeps better; it is generally preferable as a reagent except when its sparing solubility, or the presence of potassium, constitutes a drawback.

By means of the above reaction it is very easy to show the presence of traces of manganese in such substances as white marble, dissolving about a grm. in dilute nitric acid, and applying the test directly to the resulting solution. A sample of deep-sea deposit gave the reaction quite distinctly when a few milligrms. were warmed with a small quantity of sulphurous acid, and tested directly; as there was a good deal of chloride in the sample it was necessary to add silver nitrate until no further precipitation took place, and the presence of the white silver chloride did not interfere with the reaction. The same sample gave no distinct manganese reaction when tested with a sodium carbonate bead in the usual manner.

The reaction could apparently be employed colorimetrically for quantitative purposes. This was tested roughly as follows:—5 c.c. of the standard solution (containing 0·05 m.grm of Mn as $MnSO_4$), were oxidised in the usual way; 5 c.c. of the original permanganate solution (containing 0·05 m.grm. of Mn as $KMnO_4$), were acidified and diluted to the same volume. When placed in similar tubes the two solutions showed no appreciable difference as regards depth of colour. On standing for some time the original permanganate solution became decidedly paler than the other, owing to gradual reduction, so that if the reaction were to be employed for quantitative purposes it would be preferable to submit the standard comparison solution to an oxidation process similar to that carried out on the sample being tested; the standard solution could, of course, be prepared from potassium permanganate, and reduced with sulphurous acid, which would ensure that no deposition of manganese peroxide would take place on keeping the solution.

In a communication recently published in the *Proceedings of the Royal Society of Edinburgh*, describing the decomposition of ammonium persulphate solution in presence of silver salts, I have erroneously stated that chromic salts are not oxidised to chromic acid by ammonium persulphate in absence of silver. Oxidation does take place with persulphate alone, but is accelerated by the addition of a silver salt.

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NEW PROCESS FOR THE ESTIMATION OF META-CRESOL IN A MIXTURE OF CRESOLS.

By F. RASCHIG.

FOR some years past the picric acid used under the names of melinite, lyddite, &c., in the preparation of explosive materials, has been replaced by a product named cresylite. This substance is obtained by the action of nitric acid on cresol, a cheap by-product of the manufacture of carbolic acid. Cresol consists of a mixture of three isomers, ortho-, meta-, and para-cresol, and the nitrated product which is derived from it consists entirely of trinitro-*m*-cresol, the ortho- and para cresol being transformed entirely into oxalic acid at the boiling-point, and in the presence of an excess of nitric acid.

Commercial cresol contains on an average 40 per cent of ortho-cresol, 35 per cent of meta-cresol, and 25 per cent of para-cresol, and in round numbers gives 60 per cent of trinitro-meta-cresol. The operation entails a considerable loss of nitric acid through the oxidation of the ortho- and para-cresols. By fractional distillation, frequently repeated, the ortho-cresol boiling at 188° can be completely separated from the mixture of cresols, and a mixture is obtained consisting in round numbers of 60 per cent of meta-cresol, and 40 per cent of para-cresol. The boiling-point of these two products is about the same,

viz., 200° and 199·5°, so that they cannot be separated by fractional distillation. However, this mixture of the two cresols has considerable advantages over the mixture of the three cresols, so that it is more in demand, and fetches higher prices; for instance, it gives about 100 per cent of trinitro-meta-cresol, and at the same time requires less nitric acid.

From this it is apparent that the mixture of cresols will be the more valuable from the point of view of the manufacture of explosive materials, as it contains a larger proportion of meta-cresol. For this reason I have devised a method for the estimation of meta-cresol in a mixture of cresols. This method is rapid, easy to perform, does not require the use of complicated apparatus, and does not entail much expense. It is based on the already mentioned property, that the mixture of cresols treated at boiling-point with an excess of nitric acid, furnishes exclusively trinitro-meta-cresol, which, being almost insoluble in water, is easily isolated, dried, and weighed.

The following is the method of procedure finally adopted:—Exactly 10 grms. of cresol were taken, and mixed in an Erlenmeyer flask with 15 c.c. of ordinary sulphuric acid at 66° B. This was left for about an hour in a steam oven. The contents of the flask were then poured into a wide necked flask of 1000 c.c. capacity, and cooled under the tap while shaking.

By this operation the sulph-acid, which is fluid when warm, is deposited in the form of a thick syrup on the sides of the flask. 90 c.c. of ordinary nitric acid at 40° B. are then poured into the Erlenmeyer flask which was used for the sulphonation, and which still contains a little of the sulph-acid. In this manner the whole of the sulph-acid is brought into solution, and the whole of the liquid is poured into the litre flask at once. This latter is immediately shaken vigorously until the whole of the sulph-acid is dissolved, an operation which only requires about twenty seconds. The flask is then placed in the fume closet, and after about a minute a violent reaction commences; the contents of the flask begin to boil violently, accompanied by an abundant disengagement of red fumes; the solution, which has till now been clear, becomes suddenly cloudy, oily drops of trinitro-cresol separate out, and collect at the bottom of the flask; at the end of five minutes the reaction appears to have finished. The flask is, however, left for another five minutes, as the reaction is not really over sooner.

The contents are then poured into a dish containing 40 c.c. of water, and the flask is rinsed with another 40 c.c. of water. On contact with the water the oil froths up, gives off nitrous fumes, and becomes solid, forming a crystalline mass of trinitro-meta-cresol. This is allowed to cool for about two hours, when it is powdered coarsely, and collected on a filter-paper with the help of a filter-pump. The filtration is effected very rapidly; it is washed with 100 c.c. of water, dried on the filter at 95—100°, and weighed, placing a filter-paper of the same size on the other pan of the balance as tare.

With a little practice an estimation can be made in five hours, and ten or twenty analyses can easily be done concurrently.

Chemically pure meta-cresol treated in this manner gives exactly 17·4 grms. of trinitro-cresol, and it has been proved by a large number of experiments that the most variable mixtures of meta-cresol and para-cresol, and of meta-cresol and ortho-cresol, always give 1·74 per cent of trinitro-cresol per 1 per cent of meta-cresol. And again, by mixing 9 grms. of meta-cresol with 1 grm. of phenol, we obtain exactly $9 \times 1{\cdot}74 = 15{\cdot}6$ of the nitrated product.

It is probable that the picric acid derived from the phenol remains in solution under the existing conditions; but in the presence of more than 10 per cent of phenol the picric acid is precipitated with the trinitro-cresol, from which it follows that the process cannot be applied to mixtures very rich in phenol. Such mixtures, however, are not often met with commercially, and further, the presence of phenol can easily be ascertained by the boiling-point, as well as by the fact that the nitrated product, dried at 95—100°, becomes deliquescent, or turns into a soft paste, instead of remaining a solid mass.

Xylenols also, which are to be found more frequently in cresol, behave in the same manner; the nitrated product becomes liquid when warmed, and is not solidified when cooled. On the other hand, a cresol which is almost entirely volatile between 190° and 200°, that is to say, almost entirely free from phenols and xylenols, always gives, under the conditions described, a bright yellow crystalline mass, the weight of which divided by 1·74 represents the amount of meta-cresol present.

In conclusion, I should like to call attention to this point: the quantity of nitric acid used is much more than that necessary to produce complete oxidation. With cresols of average composition, containing 35 to 60 per cent of meta-cresol, 70 c.c. of nitric acid give good results. But in such a case the reaction frequently occurs so quickly that there is hardly time to properly mix the sulph-acid and the nitric acid, and to put the flask on one side; sometimes even there is such a violent reaction that the flask is blown to pieces.

I must therefore insist on the use of 90 c.c. of nitric acid, and I strongly advise the use of a flask of at least 1 litre capacity, and with a large neck. It is also indispensable to pour the whole of the nitric acid into the sulph-acid at once, for fear that a reaction should take place before the whole of the acid is in the flask.—*Zeit. für Angewandte Chemie*, 1900, p. 759.

THE SPECTRA OF RADIUM AND POLONIUM.

By G. BERNDT.

So far experiments on the spectrum of radium by Demarçay and Runge have appeared. By means of radio-active barium chloride of activity 70,000, Demarçay has discovered in the spectrum as far as $\lambda = 3500$ (Angström's units), sixteen new lines, three of which, however, he will not with certainty ascribe to radium. Runge, with his measurements which extend to $\lambda = 2400$, has only confirmed three of the strongest lines, $\lambda = 4826{\cdot}14$, $\lambda = 4682{\cdot}346$, and $\lambda = 3814{\cdot}591$. This negative result probably arose from the use of a salt of insufficient activity. Acting upon the suggestion of Prof. Dorn, I therefore undertook a new experiment on the radium spectrum in the ultra-violet, towards which the great quartz-spectrograph of the Institute afforded immense help.

I used active barium chloride of activity 240 from the Central Society of Chemical Products, Paris, and active barium bromide of De Haën, Hanover. According to the publication of Runge, the salt was fused in a platinum spiral heated to redness by electricity, by which means only a very small quantity is required.

I used about 0·03 grm. A platinum wire served as cathode. The spark was led through two Leyden jars, which were charged from a large induction apparatus. The spiral was heated by four isolated accumulators. Thus, when the spark passes, the space between the electrodes fills with vapours of the salt, and by regulating the stream from the accumulators one can at will obtain the desired quantity of gas.

If the time of exposure is not too extended the spectrum obtained will contain, besides the lines of the experimental salt, only indications of the strongest platinum lines, and only extremely few atmospheric lines.

In the spectra of the active chloride and bromide of barium, I obtained from radium lines only $\lambda = 3814{\cdot}591$ with intensity 2, in which intensities are reckoned from 6 to 1, 6 indicating the greatest intensity.

However, when I used active barium chloride of activity 1000, from the Central Society of Chemical Products, I obtained:—$\lambda = 4682{\cdot}346$, intensity 1; $\lambda = 3814{\cdot}591$, in-

tensity 4; and a new line, λ=2708·6, intensity 1. As far as λ=2100 I have found no more radium lines.

No measurements with regard to the spectrum of polonium have so far appeared. Demarçay's experiments have resulted in the discovery of no new lines. Sir W. Crookes only mentions that polonium shows bright lines in the ultra-violet.

For the photographic production I used active basic bismuth nitrate of activity 300. The spectrum obtained was at once compared with that of ordinary bismuth nitrate, bismuth, antimony, lead, copper, platinum, cadmium, and calcium chloride, and the measurements also with those of the best known spectra, and I think the following fifteen lines may be said to belong to polonium:—

Intensity.	λ.	Intensity.	λ.
1	4596·3	6	3349·2
2	4007·1	4	3191·2
4	3821·9	4	3168·2
3	3467·1	3	3162 9
2	3462·0	1	3152·2
4	3442·0	1	2977·0
6	3361·5	3	2661·9
		4	2327·3

The greatest error in the wave-lengths might be about 1·5 (Angström's units) in the visible part of the spectrum, and about 0·4 in the ultra-violet.

As far as λ=2100 I have found no more lines.

In the photographic production I was assisted by my friend Herr Henning; I wish to express my thanks to him, and above all to Prof. Dorn for his kind help.—*Physikalische Zeitschrift*, 2 Jahrgang, No. 12.

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CONCERNING LIPASE, THE FAT-SPLITTING ENZYME, AND THE REVERSIBILITY OF ITS ACTION.*

By J. H. KASTLE and A. S. LOEVENHART.

(Continued from p. 66).

Stability of Lipase.

THERE seems to be a general impression among those who have worked with this enzyme that in order to obtain active pancreatic extracts they should be prepared within a few hours after the death of the animal (Oppenheimer, "Die Fermente," 1900, 228; Shäfer, "Text-book of Physiol.," 1897, vol. i., p. 339). It is true that, as compared with many enzymes, lipase is very unstable. That it does not disappear from the gland, however, as soon as is commonly supposed, is shown by the following experiments:—Several pancreases were placed in cold storage, without antiseptic, on July 19, 1900. One c.c. of a 10 per cent aqueous extract of a fresh pancreas on July 19, in 4 c.c. of water with 0·26 c.c. of ethyl butyrate and 0·1 c.c. toluene in fifteen minutes at 40°, required 2·45 c.c. of N/20 KOH for neutralisation. It therefore hydrolysed 6·15 per cent of ethyl butyrate. On July 26 one of the pancreases was removed from the cold storage and a 10 per cent aqueous extract was prepared. It had an initial acidity of a 0·2 c.c. KOH, and 1 c.c. of it hydrolysed 2·51 per cent of ethyl butyrate under the same conditions as the first. In seven days, therefore, at a temperature of 4°, there was a falling off in lipolytic activity of about 60 per cent. Still another pancreas in which putrefactive changes had begun, was observed to possess feeble lipolytic power. Still another preparation of the pig's pancreas throws light on the stability of lipase. The attempt was made to get rid of fat in the pancreatic extract by dissecting the gland as free from fat as possible, then grinding to a stiff paste with dry sand, and drying the resulting mass by exposing it in thin layers on filter-paper for several hours at ordinary temperature in the air. The dried mass was then extracted with ligroin and dried again in the air, and finally a small quantity of thymol was ground into the siliceous mass to act as a preservative. An aqueous extract of the sand thus prepared was found to possess lipolytic activity, although it was much less active than the fresh aqueous extract of the pancreas. This preparation was made on July 12th. It was kept in the dark room in a glass-stoppered bottle. On August 17, an aqueous extract of the siliceous mass was again made, and this was found to be nearly, if not quite, as active as it was originally. With proper precautions, the extracts of the pancreas and liver can also be preserved for some time without materially losing their activity. That such is the case may be seen from the following:—

A 10 per cent aqueous extract of the pancreas was prepared on July 20th. The extract was placed in the refrigerator (temperature, 1°), and kept there for several days; its activity being tested at intervals on ethyl butyrate in the following manner:—1 c.c. of the enzyme with 4 c.c. of water, 0·1 c.c. toluene, and 0·26 c.c. ethyl butyrate were heated together in a test-tube for fifteen minutes at 40°, at the end of which time titration was made with N/20 KOH.

The following results were obtained:—

	N/20 KOH required.	Per cent of hydrolysis.
	c.c.	
Initial activity of extract	1·63	4·09
Activity of extract after forty-eight hours	1 77	4·44
Activity of extract after seventy-two hours	1·65	4·14

During seventy-two hours the initial acidity of the extract had increased from 0·1 c.c. to 0·25 c.c. N/20 KOH. This was allowed for in the above calculations. Similar results have been obtained with the aqueous extracts of the liver of the pig. A 10 per cent aqueous extract was prepared on July 24th and kept on ice for several days in a glass-stoppered bottle. Its activity towards ethyl butyrate was tested at intervals, the experiments being carried out in test-tubes, using 1 c.c. of the enzyme solution, 4 c.c. water, 0·1 c.c. toluene, and 0·26 c.c. ethyl butyrate. Temperature, 40°; duration of experiments, fifteen minutes.

	N/20 KOH required.	Per cent of hydrolysis.
	C.c.	
Initial activity of extract	1·7	4·26
Activity of extract after six hours..	2·5	6·27
Activity of extract after forty-eight hours	2·4	6·03

The increase in the activity of these extracts on standing is interesting. The above are by no means the only cases in which such an increase in activity has been observed. The best explanation of this increase in activity on standing would seem to be that during the interval a certain amount of zymogen had been transformed to enzyme. It has also been observed that glycerin extracts of the pancreas are more stable than aqueous extracts of the same activity. Some idea of the stability of the glycerin pancreatic extracts may be gathered from the following observation:—A glycerin extract was made on June 15th, 1900, and made use of in the investigation until June 23rd. Some of it was then preserved in sealed tubes in the dark room at summer temperature until August 18th, when it was still found to possess considerable lipolytic activity.

The Effect of Temperature on the Activity of Lipase.

It is well known that the activity of lipase is dependent on the temperature. According to Hanriot (*Comptes Rendus*, 1897, cxxiv., 235), the optimum temperature of the enzyme is 55°. At 60° he observed it to become con-

* From the *American Chemical Journal*, xxiv., No. 6.

siderably slower in its action, and at 72° it was found to lose its activity altogether. Towards ethyl butyrate the activity of pancreatic lipase has been found to increase more or less regularly from 0° to 40° C. Above this temperature there is a gradual falling off in activity with rise of temperature. On exposure to a temperature somewhere between 65° and 70° for five minutes, a 10 per cent pancreatic extract loses its activity altogether. The activity of hepatic lipase varies much more with the temperature between 0° and 40° C. than that of the pancreatic enzyme, as may be seen from the following experiments:—Tubes containing 4 c.c. of water, 0·1 c.c. of toluene, and 1 c.c. of a 10 per cent extract of the liver or pancreas, were kept in baths at 40°, 30°, 20°, 10°, 0°, and −10° C. respectively, for five minutes in order to let them acquire the temperature of the bath. At the end of this time, 0·26 c.c. of ethyl butyrate was added to each tube, after which the tubes were allowed to remain in their respective baths thirty minutes, when they were placed in ice-water and titrated with N/20 KOH. The following results were obtained:—

With the Pancreatic Extract.

Temperature.	N/20 KOH required.	Per cent of hydrolysis.
	C.c.	
40°	1·125	2·82
30	1·26	3·16
20	1·00	2·51
10	0·75	1·88
0	0·50	1·25

With the Hepatic Extract.

Temperature.	N/20 KOH required.	Per cent of hydrolysis.
	C.c.	
40°	4·5	11·29
30	2·375	5·96
20	2·10	5·27
10	1·55	3·89
0	0·9	2·26
−10	0·28	0·70

Similar results have been obtained by Hanriot (*Comptes Rendus*, 1897, cxxiv., 778) for serum and pancreatic lipase. He found the latter, for example, to exhibit the same activity between 15° C. and 42° C., whereas the serum lipase hydrolysed twice as much monobutyrin at 42° C. as at 15° C. In this connection it is well to bear in mind that Schmiedeberg (*Arch. f. Exp. Path. u. Pharm.*, 1881, xiv., 379) seems to have made a distinction between the enzyme of the liver which splits hippuric acid, fats, &c., and which he calls histozyme, and ordinary pancreatic lipase. On the other hand, Nencki (*Arch. f. Exp. Path. u. Pharm.*, 1886, xx., 367) has shown that the pancreas can also split hippuric acid.

On the Relative Stability of Different Ethereal Salts towards Lipase.

It is well known that other ethereal salts besides the fats are hydrolysed in the intestine. Baas (*Zeit. Physiol. Chem.*, 1890, xiv., 416), for example, found that, in the dog, salol was hydrolysed in one case to the extent of 69 per cent and in another to 43·95 per cent. Methyl salicylate to 24·75 per cent and ethyl salicylate to 21·20 per cent. Heritsch (*Centrbl. Med. Wis.*, 1875, 449) has also found that lipase could hydrolyse ethereal salts; for example, ethyl acetate. It occurred to us, therefore, that it might be interesting to measure the hydrolysis of a few of the commoner ethereal salts. Unfortunately, at this particular time, only a limited number of these were on hand of sufficient purity for the purposes of the investigation. Ethyl formate, ethyl acetate, ethyl propionate, and ethyl butyrate were therefore selected for the experiments. Tubes were prepared containing 4 c.c. of water, 0·1 c.c. toluene, and 1 c.c. 10 per cent pancreas extract. These were heated in the bath at 40° C. for five minutes. The ethereal salt to be tested was then added in the proportion of twice the molecular weight of the salt in m.grms. The tubes were then heated for fifteen minutes, when they were placed in ice-water and titrated with N/20 KOH. The following results were obtained:—

	Quantity of ethereal salt used.	N/20 KOH required.	Per cent of hydrolysis.
	Grm.	C.c.	
Ethyl formate	0·148	0·65	1·60
„ acetate	0·176	0·37	0·93
„ propionate ..	0·204	0·42	1·05
„ butyrate	0·232	1·26	3·13

A second series of experiments, exactly like the above, was tried, a more active pancreatic extract being used. The following results were obtained:—

	N/20 KOH required.	Per cent of hydroiysis
	C.c.	
Ethyl formate	0·7	1·75
„ acetate	0·7	1·75
„ propionate	1·15	2·87
„ butyrate	1·75	4·37

Both series exhibit the same order of stability, and both show that the higher the molecular weight of the acid, the more readily is its ethyl ester hydrolysed by lipase. Ethyl formate is very easily hydrolysed by pure water. This would probably account for the high values obtained with this compound.

In this connection it occurred to us that it might prove interesting, and perhaps valuable for future work upon this subject, to compare quantitatively the hydrolysing power of certain acids with that of lipase upon ethyl acetate and ethyl butyrate. Hence, normal solutions of hydrochloric, acetic, and butyric acids were made use of in very much the same way as the enzyme in the experiments described in the above. Tubes were prepared containing 4 c.c. of water and 0·176 grm. of ethyl acetate. These were then heated in the bath at 40° C. for five minutes. One c.c. of the normal acid was then run in and the tube heated for the desired length of time, at the end of which it was titrated with N/20 KOH. The following are the results obtained:—

Acid	Time.	N/20 KOH reduired.	Per cent of hydrolysis.
	Minutes.	C.c.	
Water	15	0·05	0·13
	60	0·00	0·00
Hydrochloric ..	15	2·45	6·14
	30	4·45	11·15
Acetic	15	0·05	0·13
	60	0·4	1·0
Butyric	15	None	None
	60	„	„

Second Series with N-Hydrochloric Acid.

Time.	N/20 KOH required.	Per cent of hydrolysis.
Minutes.	C.c.	
15	2·45	6·14
30	4·45	11·15
45	6·10	15·29
60	8·15	20·43
90	10·75	26·95
120	14·05	35·21

Similar experiments on the hydrolysis of ethyl butyrate by acids gave the following results:—

Conditions of Experiment.—Temperature, 40° C.; quantity of ethyl butyrate used in each experiment=0·232 grm.

Acid.	Time. Minutes.	N/20 KOH required. C.c.	Per cent of hydrolysis.
Hydrochloric ..	30	0·05	0·12
	60	0·8	2·00
	90	1·3	3·25
	120	1·5	3·75
Acetic..	30	None	None
	60	0·1	0·25
	90	0·1	0·25
	120	0·3	0·75

Several interesting conclusions may be drawn from these results, the chief of which is the remarkable difference displayed by lipase and hydrochloric acid in effecting the hydrolysis of ethyl acetate and butyrate. Both pancreatic and hepatic lipase hydrolyse ethyl butyrate considerably more rapidly than the acetate, and this notwithstanding the fact that the latter is entirely in solution under the condition of the experiment, whereas the former is not. On the other hand, normal hydrochloric acid hydrolyses the acetate about ten times as rapidly as the butyrate. As regards the cause of this remarkable difference between these two processes we are at present in the dark; it certainly offers an interesting field for further investigation.

(To be continued).

SOME PRINCIPLES AND METHODS OF ROCK ANALYSIS.*

By W. F. HILLEBRAND.

(Continued from p. 70).

VI. *Limits of Allowable Error in Summation of Analytical Results.*

As is well known, a complete silicate rock analysis which foots up less than 100 per cent is generally less satisfactory than one which shows a summation somewhat in excess of 100. This is due to several causes. Nearly all reagents, however carefully purified, still contain, or extract from the vessels used, traces of impurities, which are eventually weighed in part with the constituents of the rock. The dust entering an analysis from first to last is very considerable, washings of precipitates may be incomplete, and if large filters are used for small precipitates the former may easily be insufficiently washed.

Given the purest obtainable reagents, an ample supply of platinum, facilities for working, and a reasonably clean laboratory, there is no excuse for failure on the part of a competent chemist to reach a summation within the limits 99·75 and 100·50. Failure to attain 100 per cent in several of a series of analyses of similar nature should be the strongest evidence that something has been overlooked. Excess above 100·5 per cent should be good ground for repeating portions of the analysis in order to ascertain where the error lies, for it is not proper to assume that the excess is distributed over all determined constituents. It is quite as likely, in fact more than likely, to affect a single determination, and one which may be of importance in a critical study of the rock from the petrographic side.

VII. *Quality of Reagents.*

It is due to say that all analyses performed in the Survey laboratories have been made with the purest reagents obtainable, either by purchase in the open market, or by special preparation on the part of manufacturers, or in the laboratory. The best acids made in this country are of a high grade, and need no re-distillation except for special experiments. Ammonia has always been redistilled at short intervals; and no sodium carbonate which exceeds 2½ milligrms. of total impurity (see *prox.*, "Sodium Carbonate"), in 20 grms. (0·012 per cent) is used for the main portions, in which silica, alumina, &c., are to be estimated. For other portions, as phosphoric acid, fluorine, sulphur, a poorer grade is entirely allowable, provided it is free from the element to be determined, and from any other which might interfere with its estimation.

Hydrofluoric acid was always freshly distilled with potassium permanganate until the introduction of ceresine bottles afforded an article sufficiently pure for all but the most exacting work. Care must be exercised even yet, however, that no particles of paraffin or ceresine are floating on the acid, and that the latter is free from traces of chlorine whenever it is to be used for attacking silicates with a view to estimating chlorine (see *prox.*, "Chlorine").

Potassium bisulphate has usually been prepared in the laboratory from sulphuric acid and potassium sulphate, since it is not always to be bought of satisfactory quality. Even then the normal sulphate had first to be examined, for it has been found to contain, on different occasions, notable amounts of lead, calcium, and silica.

The phosphorus salt used for precipitating magnesium has been found to contain iron and silica, and calcium is almost always a constituent of ammonium oxalate. The latter has therefore to be purified or specially prepared, as also oxalic acid, ammonium chloride (in which latter manganese has been observed), and occasionally other reagents. Some hydrogen peroxide contains fluorine, which renders it unfit for use as a chemical reagent.

A "C. P." label is no guarantee whatever of the purity of a reagent; hence no chemicals should be taken on trust because of bearing such a label. Every new purchase should be examined, if it is one in which purity is a desideratum. In general all so-called "C. P." chemicals should at least stand the tests laid down by Krauch ("Die Prüfung der Chemischen Reagentien," 3rd Edition, Berlin, Julius Springer, 1896.

Of late years the appearance upon the market of so-called guaranteed reagents promised to meet a long-felt want. But experience has shown that with the pioneer in this line at least the guarantee amounts to nothing, the reagents being sometimes worse than the "C. P." articles emanating from sources which make no claim to special purity for their goods, and redress being unobtainable. The "guaranteed reagent" needs checking as much as any other.

VIII. *Preliminary Qualitative Analysis.*

A complete qualitative analysis of a rock, preceding the quantitative examination, is in most cases a sheer waste of time. A few constituents may now and then be specially looked for, but in general time is saved by assuming the presence of most of them and proceeding on that assumption in the quantitative analysis.

PART II.—METHODS.

I. *Introductory Remarks.*

The order hereinafter followed in describing the various chemical separations has little relation to the affinities of the constituents of the rock, but those are grouped together which can be conveniently determined in the same portion of rock powder. Thus, in the main portion are usually determined SiO_2, TiO_2, MnO, NiO, CaO, SrO, MgO, total iron, and the combined weight of all the following:—Al_2O_3, TiO_2, P_2O_5, ZrO_2, all iron as Fe_2O_3, and nearly if not quite all vanadium, as V_2O_5, also perhaps rare earths if present. In a separate portion is estimated FeO, and also the total iron, as well as BaO, if these last are desired as checks. The alkalis need a portion for themselves. In another, ZrO_2, BaO, and total sulphur are very conveniently determined. For V_2O_3 and Cr_2O_3 still another and usually much larger portion is to be used. Determinations of CO_2, C, H_2O, Fl, Cl, are all best made in separate portions of substance, though various combinations are possible, as CO_2 and H_2O, C and H_2O, or H_2O, Fl, and Cl. In fact, by a judicious selection and combination of methods a very satisfactory analysis can sometimes be

* *Bulletin of the United States Geological Survey*, No 176.

made on 4 grms. of material without omission of anything of importance, though the time consumed will be greater than if ample material is available.

As an illustration of the advantage to be gained by a little judgment in the combination of methods, the case of sulphur, barium, and zirconium may serve. Many chemists never look for the second and third of these, but by following the procedure given later on very little more labour is expended in confirming their presence or absence than that of sulphur alone.

With only occasional exceptions, nearly all the constituents mentioned (see II., *ante*), can be estimated if present in portions of powder not exceeding 1 grm. each in weight.

This is a convenient weight to take for the main portion in which silica, alumina, &c., the alkaline earths, and magnesia are to be sought; but it should, in general, be a maximum, because if larger the precipitate of alumina, &c., is apt to be unwieldy. Its weight can not often be much reduced with safety if satisfactory determinations of manganese, nickel, and strontium are to be expected. For the alkali portion one-half grm. is a very convenient weight. In general, it may be made a rule not to use more than 2 grms. for any portion which has to be fused with an alkali carbonate, as for sulphur, fluorine, and chlorine. For carbon dioxide the weight may rise to 5 grms., or even more, if the amount of this constituent is very small, without expenditure of any more time than is required by 1 grm., and with correspondingly greater approach to correctness in the result. For vanadium also a larger weight than 2 grms. is usually demanded.

II. *Specific Gravity.*
By Suspension in Water.

Ordinary Method.—This determination, when required, is best made upon one or several fragments weighing up to 20 grms. They are held together by a fine platinum wire ready for suspension from the balance, and thus held are placed in a small beaker to soak over-night in distilled water under the exhausted receiver of an air-pump, side by side with a similar beaker of water. Boiling is, of course, a much less effective means of removing air than the air-pump, and the boiling water may exert an undesirable solvent and abrading effect. In the morning the wire is attached to the balance arm, the rock fragments remaining immersed in the water; a thermometer is placed in the companion beaker of water, now likewise in the balance case, and the weight is at once taken. Both vessels of water having precisely the same temperature, it is quite unnecessary to wait for the water to assume that of the balance should it not already possess it. The fragments are now lifted out, without touching the vessel, and carefully transferred to a tared crucible or dish; the wire is removed, and at once re weighed, with the precaution that it dips just as far into the water now as when weighted. Hereby a special weighing of the wire out of water is avoided. The sample may now be dried on the water-bath, and then at 110° C. for some hours to certainly expel all absorbed water, and weighed after prolonged cooling in the desiccator. It is better to ascertain the weight of the dry rock after soaking in water than before, in order to avoid the error due to possible breaking off of a few grains between the two weighings. Should the density of the rock in air-dry condition be required, it may be left exposed to the air for a long period after drying and before weighing;* but the difference will only in exceptional cases affect the second decimal by more than a single unit. For instance, an undried rock of 2·775 specific gravity, containing in the uncrushed state the high percentage of 0·3 hygroscopic moisture, will have a density of 2·79 when dry; a rock of 2·982 specific gravity, undried, will have a density of 3·00 after removal of 0·3 per cent of moisture. The difference becomes greater as the density of the rock increases.

This method of ascertaining the specific gravity of rocks is certainly more convenient than, and for compact rocks is believed to be decidedly preferable to, that of the pycnometer, in which the fragments must be reduced to small size with consequent formation of more or less powder, which is subject to slight loss in the various manipulations. To exclude this powder and employ only small fragments would introduce a possible source of error, since it is likely to consist largely of the most easily abraded minerals, and consequently not to have the average composition of the mass. By following the instructions given above, loss of material is absolutely avoided, a decided saving in time is effected, and considerable weights can be easily employed with consequent lower probable error in the results. To vesicular rocks, however, notably certain lavas, the above procedure is, of course, inapplicable, unless the datum is desired for certain considerations in which the relative density of large rock masses as they occur in nature is sought, as for the comparison of building stones or the calculation of large known or assumed areas of particular rocks.

Penfield's Method for Mineral Fragments.—Penfield (*Am. Journ. Sci.*, 1895, Series 3, vol. l., p. 448), recommends the following modification of the suspension method as more convenient than that by the pycnometer in many cases for small fragments of minerals.

After boiling in water, the substance is transferred with water to a small glass tube about 8 m.m. by 35 m.m., provided with a fine platinum wire for suspension, This is weighed full of water in another vessel of water, and again after the removal of the mineral, the weight of which is found after drying.

This method is, of course, more applicable to homogeneous minerals than to rock fragments, and will therefore be applied in rock analysis chiefly to the determination of the specific gravity of the mineral grains separated by heavy solutions or acids.

(To be continued).

* In view of the uncertainty as to what constitutes hygroscopic water (see *post*), this course is perhaps more to be commended than the former, and seems imperative for certain zeolitic rocks. In such cases it is best to weigh the fragments before putting to soak, and afterwards to collect on a Gooch crucible the grains which may have fallen off in the water. Should no crucible of this kind be available, a paper-filter may unhesitatingly be used and incinerated with the powder, owing to the small amount of which the error due to loss of even all its water during ignition is quite negligible.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Annual General Meeting, February 8th, 1901.

Mr. G. GRIFFITH, Vice-President, in the Chair.

THE report of the Council was read and adopted.

Professor Willard Gibbs and Dr. Rudolph Kœnig were elected to the two vacant Honorary Fellowships of the Society.

The following Officers and Council were elected for the ensuing year:—

President—Prof. S. P. Thompson.

Vice-Presidents (Members who have filled the office of President)—T. H. Blakesley, C. V. Boys, Prof. J. D. Everett, and J. Walker.

Secretaries—H. M. Elder and W. Watson.

Foreign Secretary—Dr. R. T. Glazebrook.

Treasurer—Prof. H. L. Callendar.

Librarian—W. Watson.

Other Members of the Council—Prof. Armstrong, W. R. Cooper, G. Griffith, E. H. Griffiths, Dr. R. A. Lehfeldt, S. Lupton, Prof. Perry, Dr. Porter, W. A. Price, and R. Threlfall.

Prof. S. P. THOMPSON then took the chair and delivered an Address.

In opening, the President gave in detail the various

ways in which the aim of the Physical Society to promote the progress and study of physics has been accomplished during the twenty-six years of the Society's existence.

Referring to the election of two Honorary Fellows, Prof. Thompson said they had added to their roll two men distinguished in very different walks of physics. Prof. Willard Gibbs is a United States mathematical physicist whose work in thermodynamics, elastic solid theory of light, and other specialised subjects, is of the highest order, and is valued for its beauty and profundity. Dr. Rudolph Kœnig, of Paris, is known as a maker of acoustical instruments—of perfect standard tuning-forks in particular. He has, however, found time to extend the borders of acoustics, and to him we owe the manometric flames, the wave-syren, and other instruments of research. He has also published work on the facts about the combinations of pure tones.

The President appealed to all teachers of physics in the country to make use of the Society and give it their active support. It was mainly in the interest of teachers and students that the Society undertook the publication of *Science Abstracts*. By means of the *Abstracts* teachers have at hand the latest information on the subject, and can thus continually supplement their text-book knowledge. Every teacher from time to time devises new or improved modes of presenting his subject. At the Physical Society, the Fellows always welcome contributions of this kind, even although there may be little of actual novelty in the principles so illustrated. The routine work and administrative duties of teachers, although hampering their usefulness to science and diminishing their fruitfulness, prevents their attention, without intermission, to one subject, and produces a direction of thought over various domains of physics which is to be welcomed rather than deplored. It has been the custom for Fellows of the Physical Society to bring models to illustrate physical principles. This practice of using models is regarded by our Continental brethren as a peculiarly English matter, and one that shows a sort of mental constitution they do not quite understand. Models have become a part of our mental furniture. It never occurs to us that there is anything unusual in the habit. Faraday has used them in connection with the electrostatic field surrounding charged bodies. Lord Kelvin has made models to convey his ideas of elasticity, of the elastic solid theory of matter, and of the constitution of matter itself. Maxwell's models of heterogeneous dielectrics and the mutual induction between two circuits are well known. These models are useful for teaching purposes, and for enabling one to grasp that which in its nature is abstract, by contemplating the representation of it or its analogue in the concrete. The French physicist cannot understand a complicated phenomenon until he has reduced it to a mathematical equation. The British physicist must construct a model which will produce mechanically the analogous operation. Both methods are right, but—judging by their fruitfulness—the method of Faraday has advantages over that of Poisson.

Referring to the new Teaching University of London, the President said that now was the time for Fellows to offer suggestions for the teaching of physics.

An Ordinary Meeting of the Society was then held.

A paper on "*A Mica Echelon Grating*," by Prof. R. W. Wood, was read by Mr. Watson.

This grating occupies a position midway between an ordinary grating and an echelon with thick plates. A number of sheets of mica were examined with the interferometer, and one selected over a considerable portion of which the fringes were straight and unbroken. This portion was marked off and cut up into rectangles. The mica was about 0·05 m.m. thick, and the retardation of one of the rectangles was found to be fifty wave-lengths for sodium light. Nine of these rectangles were used to form the grating, and they were put in position under a microscope and cemented together at the edges with sealing wax. The grating space was 0·5 m.m. The battery was mounted on a square of cardboard over a rectangular opening of the same size, a clear space, 0·5 m.m. wide, being left to serve as the first grating line of zero retardation; the number of lines was therefore ten. The resolution of the sodium lines was beyond the power of the instrument, but the yellow mercury lines were easily separated. The distance between the lines was one-third of the distance between the spectra. For the sake of comparison, a grating of the same spacing and number of lines was ruled on a piece of smoked glass, and it was found that in the first order the grating was unable to separate the extreme red and blue ends of the spectrum. The Zeeman effect can be shown with an echelon made of four interferometer plates, the light being the green rays from a mercury tube.

The Society then adjourned until February 22nd.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, del'Académie des Sciences. Vol. cxxxii., No. 3, January 21, 1901.

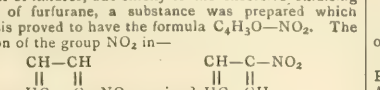
Properties of Sodium Dioxide.—M. de Forcrand.—The author criticises G. F. Jaubert's paper, which appeared in the last numbers of the *Comptes Rendus*. He announces that the heat of formation and solution of Na_2O_2 have already been found, and the properties of this substance described in detail.

Compounds of Ammonia Gas with Aluminium Chloride.—E. Baud.—The author establishes the fact that aluminium chloride forms with ammonia at least four compounds:—(1) $Al_2Cl_6.2NH_3$, which is a very stable substance, capable of being distilled at about 450° without undergoing decomposition; (2) $Al_2Cl_6.10NH_3$, also a very stable substance, which is dissociated under atmospheric pressure at about 380°; (3) $Al_2Cl_6.12NH_3$, a substance which dissociates under atmospheric pressure at about 180°; (4) finally, the compound probably having the formula $Al_2Cl_6 + 18NH_3$, which is very easily dissociable, and which can only be obtained at temperatures approaching the liquefying-point of ammonia gas.

The Isolation of Yttria, Ytterbia, and New Erbia.—G. and E. Urbain.—The authors, in a previous paper, described a new method of fractionating the yttria earths by the crystallisation of their ethyl sulphates. In the most soluble portions were found yttria, new erbia, and ytterbia. These fractions did not contain a trace of the earths of the lanthanum group, and apparently contained no earths of the samarium and gadolinium groups. This latter group was eliminated by this method of fractionation before holmia, dysprosia, and new holmia. Since that time, the authors have prepared large quantities of these mixtures, and have examined methods of separating earths of the same group. The method which has given the best results is still that of the partial decomposition of the nitrates by heat. The crude rare earths were first subjected to ten crystallisations as ethyl sulphate. The final mother-liquor was found to contain yttria, erbia, ytterbia, and a trace of thoria. This mixture was then transformed into nitrate, and after about twenty fusions the authors obtained in the least basic portion a mixture of ytterbia and thoria. The thoria was then separated by Wyrouboff and Verneuil's method. The atomic weight of the remaining ytterbia was found to be 172·6, and the spectrum of this ytterbia was absolutely free from absorption bands. Yttria and erbia were obtained in almost as pure a form.

An Arsenide and a Chloro-arsenide of Tungsten.—Ed. Defaçoz.—It is known that phosphoretted hydrogen reacts on tungsten hexachloride, giving a definite compound. The author finds that hydrogen arsenide reacts on the same hexachloride, and a new compound is formed, having the formula WAs_2. Also liquid hydrogen arsenide acts on the hexachloride, giving in this case a chloro-arsenide, W_2AsCl_2, a substance of a bluish black colour in the form of little crystals similar to those of the hexachloride. This compound is very hygroscopic, and is decomposed slowly when left in contact with air.

Nitrofurfurane.—R. Marquis.—After a series of researches on the preparation of furfuranamine, $C_4H_3O{-}NH_2$, by an indirect method, the author now proceeds to prepare the nitrated derivative. After a number of failures, due chiefly to the excessive oxidising power of furfurane, a substance was prepared which analysis proved to have the formula $C_4H_3O{-}NO_2$. The position of the group NO_2 in—



being as yet undetermined.

Absorption-spectra of the Indophenols.—Paul Lemoult.—The author succeeds in obtaining the mobility of the red band in the series of the indophenols, and in discovering the causes which provoke its displacement. The colouring-matters having a discontinuous absorption-spectrum show a red band, of which the centre is fixed (for a molecular dilution and an invariable thickness) as long as the molecule is only complicated with non-significative substitutions, whilst the middle of this band is very sensibly displaced, when the number of tertiary nitrated groups is modified.

New Organo-metallic Compounds of Mercury.—Auguste Lumière, Louis Lumière, and M. Chevrotier.—Mercury-phenoldisulphonate of sodium, prepared by the decomposition of the sodium salt of phenoldisulphonic acid, is obtained in the form of a white amorphous powder, containing about 40 per cent of mercury and very soluble in water. Solutions of this substance lose their metallic taste and even the saline taste of sodium salts; they are not precipitated by soda, hydrochloric acid, or ammonium sulphide.

Methods of Formation and Preparation of Propylbenzene.—F. Bodroux.—When trimethylene bromide acts on benzene in presence of aluminium chloride, the author obtains, at the same time as symmetric diphenylpropane, a notable quantity of propylbenzene. The presence of this hydrocarbide proves, without doubt, the decomposition of a part of the diphenylpropane by the aluminium chloride. Bromine reacts on this substance at 160°, giving rise to dibromophenylallyle, $C_6H_5{-}CHBr{-}CHBr{-}CH_3$. Bromine itself, in presence of aluminium bromide reacting on propylbenzene, gives pentabromopropylbenzene. This latter substance is accompanied by a very small quantity of hexabromobenzene.

Purification of Air by Soil.—Auguste Gérardin.—The authors experiments establish the following facts:—(1) The earth is permeable to the air, and its permeability is independent of its composition; (2) the resistance of the earth to the passage of air is proportional to the thickness of the filtering layer; (3) the resistance of the earth to the passage of air is proportional to the quantity of water which moistens it.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxiii., Nos. 16 and 17.

The Action of Iodides and of Hydriodic Acid on Sulphurous Acid.—J. Volhard.—The author has found that hydriodic acid causes the decomposition of sulphurous acid into sulphuric acid and sulphur, without its elements taking part in the reaction; in fact, the hydriodic acid remains unchanged after the decomposition of the sulphurous acid, so that a minimum amount of the former suffices for the decomposition of an infinite quantity of the latter. The reaction takes place the quicker as the solutions are more concentrated. The author attributes this catalysis to the concurrence of two simultaneous reactions: the sulphurous acid oxidises the hydrogen of the hydriodic acid and sets free sulphur and iodine, another portion of iodine, while decomposing the water, causes the oxidation of the sulphurous acid into sulphuric acid, at the same time regenerating the hydriodic acid, and thus the series of reactions goes on:—

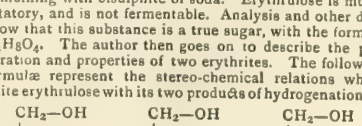
$$SO_2+4HI=2H_2O+4I+S,$$
$$2SO_2+4H_2O+4I=2SO_4H_2+4HI,$$
$$3SO_2+2H_2O+4HI=2SO_4H_2+S+4HI,$$

or, abstracting the elements of water, $3SO_2=2SO_3+S$.

The Reduction of Tungstic Anhydride by Zinc. Preparation of Pure Tungsten.—Marcel Delépine.—Already inserted in full.

On some Phosphoric Ethers.—J. Cavalier and E. Prost.—The authors have prepared some new derivatives of normal propylic, isopropylic, and isobutylic alcohols, viz., their phosphatic ethers, which are analogous to those of the methylic and ethylic alcohols and are prepared in the same manner. For the neutral ethers, PO_4R_3, corresponding quantities of triargentic phosphate and alcoholic iodide are caused to react together by gently heating. Take up with ether and distil, first on the water-bath and then *in vacuo*. The two acid ethers are obtained simultaneously during the reaction of phosphoric anhydride on anhydrous alcohol. On taking up with water, a solution is obtained which contains the three acids, PO_4R_2H, PO_4RH_2, and PO_4H_3. These are easily separated by forming salts of barium neutral to phthalein, and taking advantage of their great difference of solubility in water. The properties of these bodies are then described in full.

The Oxidation of Erythrite by the Bacteria of Sorbose. Production of Two New Sugars, *d*-Erythrulose and *d*-Erythrite.—Gabriel Bertrand.—Erythrulose is obtained in the following manner:—A decoction of brewer's yeast, containing 5 grms. of soluble matter per litre, is treated with 4 per cent of erythrite, then placed in portions 2·5 c.m. in thickness in several large matrasses with wide necks. These are closed with plugs of cotton-wool and sterilised at 110°; they are then infected and kept at a temperature of 28—29° for three weeks, when the transformation of the erythrite is complete. The liquid is then separated and exactly saturated with baryta-water; it is then evaporated to a syrup, which is gradually taken up with half a litre of absolute alcohol to which two volumes of dry ether are then added. A brown precipitate is formed, which is treated again with alcohol and ether, and the solutions, added together and filtered, are evaporated *in vacuo*; in this manner a syrup very rich in erythrulose is obtained. It can be further purified by taking advantage of its property, very rare among sugars, of combining with bisulphite of soda. Erythrulose is multirotatory, and is not fermentable. Analysis and other data show that this substance is a true sugar, with the formula $C_4H_8O_4$. The author then goes on to describe the preparation and properties of two erythrites. The following formulæ represent the stereo-chemical relations which unite erythrulose with its two products of hydrogenation:—



l-Erythrite. *d*-Erythrulose. *d*-Erythrite.

It must be concluded that the sugar obtained by the action of the bacteria of sorbose on erythrite is *d*-erythrulose.

Products of Condensation of Dichlorophthalic Anhydride with Diethylaniline.—E. C. Severin.—By substituting diethylaniline for dimethylaniline a series of bodies entirely comparable with the methylic series is obtained; these are all fully described in a somewhat lengthy paper.

Action of Chloride of Aluminium on Camphoric Anhydride.—G. Blanc.—Already noticed.

The Campholytic and Isolauronolic Acids.—G. Blanc.—An examination of the nature of the isomerism of these two acids.

Diphenylcarbazide: a very Sensitive Reagent for some Metallic Compounds, such as those of Copper, Mercury, Iron (Per-salts), Chromic Acid. — P. Cazeneuve.—Already noticed.

MISCELLANEOUS.

Alkalimetric Method for the Estimation of the Salifiable Alkaloids.—H. M. Gordin.—We prepare N/20 solutions of hydrochloric acid and potash, as well as an iodo-iodised solution (I 10 grms., KI 15 grms., H_2O to 1000 c.c.), and then proceed in the following manner:— 0·20 grm. of morphine, dried at 120°, is placed in a 100 c.c. flask, 30 c.c. of N/20 HCl are added, then the iodo-iodised liquor until the precipitate is no longer formed. The liquid is diluted up to 100 c.c., shaken well to collect the precipitate, and filtered. 50 c.c. are taken and decolourised with 10 per cent hyposulphite of soda; the acidity of the liquor is then titrated with N/20 soda, in the presence of phthalein. We know by difference the number of c.c. of N/20 HCl which corresponds to 0·20 of morphine, and consequently, the proportion of this base which corresponds to 1 c.c. of N/20 HCl. The corresponding quantities of the other alkaloids can be deduced from their molecular weights. 1 c.c. N/20 HCl=0·0137 of anhydrous morphine, 0·0184 of hydrastine, 0·0160 of strychnine, 0·0102 of crystallised caffein, 0·0139 of atropine, and 0·0146 of cocaïne.—*Berichte*, vol. xxxii., p. 287.

MEETINGS FOR THE WEEK.

MONDAY, 18th.—Society of Arts, 8. (Cantor Lectures). "The Bearings of Geometry on the Chemistry of Fermentation," by W. J. Pope.
—— Royal Institution, 3. "The Origin of Vertebrate Animals," by Arthur Willey, M.A., D.Sc.
—— Society of Chemical Industry, 8. Discussion on "Occurrence and the Detection of Arsenic in Manufactured Products."
TUESDAY, 19th.—Royal Institution, 3. "Practical Mechanics" (Experimentally treated), by Prof. J. A. Ewing, M.A., F.R.S., M.Inst.C.E.
—— Society of Arts, 4.30. "The Crisis in China—its Causes and Solution," by By Jos. Walton, M.P.
WEDNESDAY, 20th.—Society of Arts, 8. "Some Features of Railway Travelling—Past and Present," by Frederick McDermott.
—— Royal Institution, 3. "Vocal Music, its Growth and Decay," by F. Corder, F.R.A.M.
—— Microscopical, 7.30. Exhibition of Bacteria and Blood Parasites, by Mr. C. Beck.
THURSDAY, 21st.—Chemical, 8. "Isomeric Hydrindamine Mandelates and Phenylchloracethydrindamides" and "Isomeric Benzylhydrindamine Bromocamphorsulphonates and some Salts of *d-l*-Hydrindamine," by F. Stanley Kipping and H. Hall. "Condensation of Phenols with Esters of the Acetylene Series—IV., Benzo-γ-pyrone and its Homologues," by S. Ruhemann and H. W. Bausor. "Constitution of Bromocamphoric Anhydride and Camphanic Acid," by A. Lapworth and W. H. Lenton. "The Action of Acetylchlor- and Acetylbrom-aminobenzenes on Amines and Phenylhydrazine," by F. D. Chattaway and K. J. P. Orton.
—— Royal Institution, 3. "Society in France before the Revolution," by the Rev. Henry Grey Graham.
FRIDAY, 22nd.—Physical, 5. "How Air subjected to X Rays Loses its Discharging Property, and How it Discharges Electricity," by Prof. Emilio Villari. "On the Propagation of Cusped Waves and their Relation to the Primary and Secondary Focal Lines" and "On Cyanine Prisms, and a New Method of Exhibiting Anomalous Dispersion," by Prof. R. W. Wood.
—— Royal Institution, 9. "Metals as Fuel," by Sir W. Roberts-Austen, K.C.B., D.C.L., F.R.S.
SATURDAY, 23rd.—Royal Institution, 3. "Sound and Vibrations," by the Rt. Hon. Lord Rayleigh, F.R.S., &c.

ERRATUM.—The publisher of the new "Inorganic Chemistry," reviewed on p. 70, col. 2, is "Thomas Murby," and not, as there given, "Thomas Murray."

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THE CHEMICAL NEWS.

Vol. LXXXIII., No. 2152.

ON THE

PROTEID REACTION OF ADAMKIEWICZ, WITH CONTRIBUTIONS TO THE CHEMISTRY OF GLYOXYLIC ACID.*

By F. GOWLAND HOPKINS, M.A., M.B., University Lecturer in Chemical Physiology, and SYDNEY W. COLE, B.A., Trinity College.

(Concluded from page 75).

IV. *Remarks on the Colour Reaction; Spectroscopic Phenomena.*

Adamkiewicz (*loc. cit.*, p. 158), observed that the colour produced in the reaction varies from red to violet, the blue element increasing with increase in the amount of acetic acid employed. When glyoxylic acid in aqueous solution is used, unless the solution be very dilute, the colour partakes more of a blue shade than is usually seen with ordinary specimens of acetic acid. But after concentrating the reactive substance of the latter by fractional distillation (*supra*) or upon large dilution of the glyoxylic acid solution, the colours obtained become identical. The spectroscopic absorption is identical whichever reagent is employed.

When sulphuric acid is added to a solution of proteid in acetic acid wholly free from glyoxylic acid, a considerable amount of charring occurs, and the mixture becomes somewhat fluorescent. When, under similar circumstances, very little glyoxylic acid is present, the reddish colour obtained is still associated with fluorescence. But, when sufficient of the glyoxylic acid is present, whether in acetic or aqueous solution, to combine with the whole of the proteid product concerned in the reaction, there is complete absence of charring and little or no fluorescence. The solution becomes of a pure violet-blue colour.

The coloured product of the Adamkiewicz reaction is usually stated to show an absorption band between *b* and F in the position of the urobilin band; and Krukenberg described another between D and E. Salkowski found the former to be inconstant, and we are convinced that the latter alone is proper to the real product of the colour reaction: the former, when seen, being due to some accessory effect of the strong acids upon proteids. It is never seen in the original form of the reaction unless the acetic acid employed is greatly deficient in reactive power, and it is not observed with glyoxylic acid. The other band is always present, and is identical after the use of a satisfactory specimen of acetic acid and when a solution of glyoxylic acid is used.

The band shrinks rapidly from its more refrangible edge on dilution of the solution, its redward edge shifting but little.

The following readings show the correspondence seen after employing acetic acid as obtained in the market (but with its active substance concentrated by distillation), and that seen after the use of glyoxylic acid in aqueous solution. The strengths were so arranged that, before dilution, the colour of each solution appeared to be of the same intensity. Witte's peptone was the proteid employed to obtain the reaction:—

	Acetic acid.	Aqueous glyoxylic acid.
Strong	λ 480—λ 625	λ 480—λ 630
Diluted with an equal volume of sulphuric acid	λ 495—λ 625	λ 495—λ 625
Diluted with thrice its volume of sulphuric acid	λ 530- λ 610	λ 530—λ 615

V. *Other Sources of the Reactive Substance.*

Of the typical two-carbon compounds—glycol, glycollic aldehyde, glycollic acid, glyoxal, glyoxylic acid, and oxalic acid—none but the aldehyde-acid (glyoxylic acid, HCO.COOH or $CH(OH)_2.COOH$), gives the smallest indications of yielding a colour reaction with proteid on addition of sulphuric acid. It would seem that the reaction is not common to aldehyde-acids, as glycuronic acid, $HCO(CH.OH)_4COOH$, gives wholly negative results. Again, a ketonic acid so closely related to glyoxylic acid as pyruvic acid, $CH_3.CO.COOH$, gives no indication of a reaction.

Glyoxylic acid stands, of course, alone in containing the aldehydic and carboxylic groups in juxtaposition. Our observations are far from being complete enough to enable us to assert that a reaction with proteid of the special type under consideration depends essentially upon this particular structure. But the preliminary observations we have made tend to give some probability to this view. At least it may be said that hitherto we have never obtained a reaction except with products in which either glyoxylic acid has been shown to be present, or in which its presence is extremely probable.

For instance, we have found that mesoxalic acid (prepared from barium alloxanate) in aqueous solution gives with proteid and sulphuric acid a perfectly typical Adamkiewicz reaction; but under the conditions employed we have found that a portion at least of the mesoxalic acid present loses carbon dioxide, so that it is in the highest degree probable that glyoxylic acid is in this case also the substance which reacts.

Pyruvic acid gives, as we have said, no trace of a reaction, but the product of its oxidation by peroxide of hydrogen undoubtedly reacts. *Paralactic acid*, itself inactive, yields also an active product on oxidation by Fenton's method at the temperature of the water-bath. These two cases go together, as Fenton and Jones have shown that lactic acid yields pyruvic acid when oxidised at 0° in the presence of ferrous iron. It seems extremely probable that the oxidation of the pyruvic acid at the higher temperature yields mesoxalic acid, and that the reaction obtained is therefore due in each case to glyoxylic acid.

One abundant source of a reactive substance is found in the oxidation of *glycerin* by Fenton's method, carried out at the temperature of the water-bath. *Glyceric acid* yields the substance under like conditions; and, as Fenton and Jones (*Journ. Chem. Soc.*, 1900, vol. lxxvii., p. 72), have shown that glyceric acid, when the oxidation is carried out in the cold, gives a product which is almost certainly either hydroxy-pyruvic acid or the tautomeric substance dihydroxyacrylic acid, the facts here quite probably fall into line with those just enumerated. The substance which reacts with proteid is only obtained in quantity in these cases when the oxidation is carried out at higher temperatures than those used by Fenton, and if the oxidised products are distilled, it is always found that the distillate gives the reaction.

When *dextrose* solutions are boiled with peroxide in the presence of ferrous salts a substance is formed, volatile with steam, which yields the proteid reaction abundantly. Preliminary observations that we have made leave little doubt that this is glyoxylic acid itself.

If it should prove that the reaction is, as a matter of fact, peculiar to glyoxylic acid, it certainly forms a very delicate test for that substance.

* From the Physiological Laboratories, Cambridge. A Paper read before the Royal Society, February 7, 1901.

VI. *Glyoxylic Acid Solutions a Practical Test for Proteids.*

By replacing the acetic acid of the Adamkiewicz reaction by weak aqueous solutions of glyoxylic acid a very beautiful and reliable test for proteids is obtained. The colour reaction is brilliant, and the test is, of course, subject to none of the uncertainty inseparable from the use of acetic acid.*

In preparing such a test solution, there is usually no need to separate the glyoxylic acid from associated products. Excellent test solutions may be made by oxidising upon the water-bath, in the presence of small quantities of ferrous iron, either weak solutions of tartaric acid or mixtures of glycerin and water, great care being taken to ensure that no trace of free peroxide remains at the close of the operation. But we strongly recommend the use of reduced oxalic acid for the purpose, as a solution can be prepared with great ease, and almost without regard to conditions. In a moderately strong solution of oxalic acid a few lumps of sodium amalgam are placed, the amount taken of the latter being less than sufficient to neutralise the acid. When the evolution of hydrogen has ceased, the solution is poured off from the mercury and filtered. It will be found, even after large dilution, to yield an intense reaction with proteids if used instead of acetic acid under the familiar conditions of the Adamkiewicz test. The proteid, or the proteid solution to be tested, should be first added to the reagent, and then strong sulphuric acid poured down the side of the test-tube. The reaction may be first observed at the junction of the fluids, and the latter subsequently mixed. At least one-third volume of sulphuric acid should be used, but the quantity may be almost indefinitely increased. There is no tendency to charring.

Summary.

The proteid reaction described by Adamkiewicz is not a furfurol reaction, but depends upon the presence of small quantities of an impurity in the acetic acid employed. Some specimens of acetic acid yield no reaction, and all may be deprived of chromogenic power by distillation.

The substance essential to the reaction is glyoxylic acid.

Small quantities of glyoxylic acid are produced during the oxidation of acetic acid by hydrogen-peroxide in the presence of ferrous iron. Under the conditions used in this research, part of the glyoxylic acid thus formed is split up, yielding formaldehyde.

Glyoxylic acid is slowly formed when acetic acid stands in the air, and more rapidly in the presence of ferrous iron and under the influence of direct sunlight. Most specimens of acetic acid contain small amounts of glyoxylic acid as an admixture.

A dilute aqueous solution of glyoxylic acid, which may be readily prepared by the reduction of oxalic acid with sodium amalgam, forms an admirable test for proteids when used instead of acetic acid under the ordinary conditions of the Adamkiewicz test.

In carrying out this investigation we have been led to employ extensively the method of oxidation described by H. J. H. Fenton, and as a result we have in some degree trenched upon the systematic study of the oxidation of organic acids which he has in hand. It is with his consent that such of our observations are published.

The expenses of the research were met by a grant awarded to one of us by the Government Grant Committee of the Royal Society.

* It is certainly rare to find a specimen of acetic acid which yields no reaction, though many contain too little glyoxylic acid to give a satisfactory colour. It seems to be possible, however, that there have been cases of a proteid derivative being found to yield no Adamkiewicz reaction, in which the negative result was really due to the acetic acid employed. We have, for instance, prepared and carefully purified the primary albumoses from Witte's peptone by the method of E. P. Pick (*Zeitsch. f. Physiol. Chem.*, 1899, vol. xxviii., p. 219). Unlike this observer, we have found these products to yield a marked Adamkiewicz reaction; and with all reserve, we venture to suggest that the acetic acid employed by Pick at this stage of his observations may have chanced to be free from chromogenic power.

CONCERNING LIPASE, THE FAT-SPLITTING ENZYME, AND THE REVERSIBILITY OF ITS ACTION.*

By J. H. KASTLE and A. S. LOEVENHART.

(Continued from p. 80).

On the Effect of Antiseptics on Lipase.

For certain parts of the work it was necessary to exercise considerable care in the choice of an antiseptic. It was therefore thought desirable to study the effect of a number of the commoner antiseptics on this enzyme. Such a study seemed all the more desirable inasmuch as but few, if any, systematic studies of the action of antiseptics in general on enzymes have been undertaken. Some observers have studied the effect of one particular substance, and others that produced by another, but few, if any, general comparisons of the action of antiseptics have ever been made. The first series of experiments was made with salicylic acid. Tubes were prepared containing water (quantity indicated in the following table), 0·1 c.c. of toluene, 1 c.c. of 20 per cent pancreas extract, together with a certain amount of salicylic acid, varying in the amount from 0·1 to 1 c.c. of a 0·5 per cent solution. The tubes were heated for five minutes at 40° C., when 0·26 c.c. of ethyl butyrate was added. The tubes were then allowed to remain in the bath at 40° for fifteen minutes, when they were removed and titrated with N/20 KOH.

Quantity of water used.	Quantity of a 0·5 per cent solution salicylic acid used.	N/20 KOH required.	Per cent of hydrolysis.
C.c.	C.c.	C.c.	
4·0	None	2·25	5·65
3·9	0·1	2·12	5·32
3·5	0·5	1·4	3·51
3·0	1·00	0·2	0·50

This series exhibits a regular decrease in the activity of the enzyme in the presence of increasing amounts of salicylic acid.†

In the second series of experiments the following substances were employed in solution in the proportion of 1 to 1000:—Silver nitrate, mercuric chloride, hydrocyanic acid, salicylic acid, thymol, and sodium fluoride. Tubes were prepared containing 4 c.c. of water or of the solution of the antiseptic to be tested and 1 c.c. of the enzyme (15 per cent pancreatic extract). The tubes were then heated for five minutes at 40°, at the end of which time 0·26 c.c. of ethyl butyrate was added to each tube. The tubes were then allowed to remain in the bath at 40° for fifteen minutes, at the end of which time they were titrated with N/20 KOH. The following are the results:—

Substance used.	N/20 KOH required.	Per cent of hydrolysis.
	C.c.	
Water	1·8	4·52
Hydrocyanic acid ..	1·7	4 27
Thymol	1 6	4·02
Mercuric chloride ..	0·3	0·75
Silver nitrate	0·15	0·38
Salicylic acid	None	None
Sodium fluoride	None	None

In the third series of experiments, the following substances were tried:—Potassium cyanide, ammonium oxalate, and toluene. These substances were used in a solution containing 1:1000. Tubes were prepared containing 4 c.c. of water, or of the solution of the antiseptic to be tested, and 1 c.c. of pancreatic extract. These were heated at 40° for five minutes, when 0·26 c.c. of ethyl butyrate was added to each tube. They were allowed to

* From the *American Chemical Journal*, xxiv., No. 6.

† An investigation of the power of salicylic acid to prevent the fermentation of wine-must by Neubauer gave similar results. See *Journ. Prakt. Chem.*, [2], xi., 1.

remain in the bath at 40° C. for fifteen minutes and then they were titrated with N/20 KOH. The following are the results :—

Substance used.	N/20 KOH required.	Per cent of hydrolysis.
	C.c.	
Water	1·4	3·51
Ammonium oxalate	1·25	3·14
Toluene	1·15	2·89
Potassium cyanide	0·3	0·75

The effect of antiseptics 1 : 1000 was next tried on a 10 per cent hepatic extract, which had been made up originally without an antiseptic. Ethyl acetate was employed in this series of experiments. Tubes were prepared containing 3 c.c. of water, 1 c.c. of enzyme, and 1 c.c. of the antiseptic. These tubes were then heated at 40° for fifteen minutes, after which 0·19 c.c. ethyl acetate was added. The tubes were then allowed to remain in the bath at 40° for thirty minutes, when they were titrated with N/20 KOH. The following are the results :—

Substance used.	N/20 KOH required.	Per cent of hydrolysis.
	C.c.	
Water	2·65	6·62
Toluene	2·90	7·25
Chloroform	2·50	6·25
Hydrocyanic acid	2·30	5·75
Mercuric chloride	2·00	5·00
Thymol	1·85	4·63
Silver nitrate	1·60	4·00
Salicylic acid	1·50	3·75
Osmic acid	1·45	3·63
Sodium fluoride	0·10	0·25

After titration the tubes were allowed to stand at ordinary temperature (30° C.) for an hour and a half, when they were titrated a second time, with the following results :—

Substance used.	N/20 KOH required.	Per cent of hydrolysis.
	C.c.	
Water	3·02	7·55
Toluene	3·90	9·75
Chloroform	3·65	8·82
Hydrocyanic acid	3·40	8·50
Mercuric chloride	2·70	6·75
Thymol	3·00	7·50
Silver nitrate	2·20	5·50
Salicylic acid	3·05	7·60
Osmic acid	2·45	6·12
Sodium fluoride	0·20	0·50

Finally, the attempt was made to determine the effect of a number of antiseptics on liver and pancreatic extracts of about the same activity towards ethyl butyrate. Therefore a 10 per cent liver extract was compared with a 20 per cent pancreatic extract under the following conditions :—Tubes were prepared containing 3 c.c. of water, 1 c.c. of the antiseptic (1 : 1000), and 1 c.c. of the enzyme. These were heated at 40° C. for five minutes to give the antiseptic a chance to act. Then 0·26 c.c. ethyl butyrate was added, and the tubes allowed to remain in the bath at 40° C. for fifteen minutes, when they were removed and titrated with N/20 KOH. The results are given in Tables A and B.

It is believed that in the last two series of experiments a mistake was made in not allowing the antiseptic to remain in contact with the enzyme for a greater length of time in order that the effect of the weaker of them might have been more pronounced.

It will be observed that certain of the antiseptics tested exert the same effect on both the pancreatic and liver extracts; for example, chloroform is almost without effect, and thymol, hydrocyanic acid, and sodium fluoride each reduces the activity of the two extracts to the same extent. On the other hand, some of the substances used behave differently towards the two enzymes. For example, while strychnine sulphate and phenol both reduced the activity of the pancreatic extract about 30 per cent, they were without effect on the activity of the liver extract. On the other hand, osmic and salicylic acids seem to exert a more detrimental effect on the hepatic than on the pancreatic lipase. While perhaps not conclusive, these results are suggestive at least, for, if after repeated trials, it were to turn out that several substances exerted a different effect upon liver and pancreatic lipase, it would probably indicate that the two enzymes are in reality different substances. Upon pancreatic lipase especially, nearly all kinds of substances seem to exert a harmful effect. Towards a number of them, on the other hand, the lipase of the liver is more stable. Generally speaking, the more germicidal and antiseptic the substance, the greater its power to inhibit and destroy the activity of lipase. Substances like silver nitrate, mercuric chloride, salicylic acid, and osmic acid exert a more pronounced detrimental effect than the weaker antiseptic substances —such as toluene, chloroform, thymol, &c. One point of especial interest in this connection is the remarkably destructive action of sodium fluoride on lipase. In all of our tests, this substance has been found to exert the most destructive influence upon lipase of any substance yet

TABLE A.

Series with 10 per Cent Liver Extract.

Substance used.	N/20 KOH required.	Per cent of hydrolysis.
	C.c.	
Water	3·4	8·54
Formic aldehyde	3·7	9·29
Iodoform	3·5	8·78
Cocaine hydrochloride	3·5	8·78
Strychnine sulphate	3·45	8·66
Phenol	3·45	8·66
Toluene	3·3	8·28
Chloroform	3·25	8·16
Mercuric chloride	3·2	8·03
Bromoform	2·9	7·28
Thymol	2·9	7·28
Hydrocyanic acid	2·75	6·90
Salicylic acid	2·60	6·53
Silver nitrate	2·55	6·40
Osmic acid	2·00	5·02
Sodium fluoride	0·45	1·13
Hydrochloric acid	0·25	0·63
Hydrofluoric acid	0·25	0·63

TABLE B.

Series with 20 per Cent Pancreatic Extract.

Substance used.	N/20 KOH required.	Per cent of hydrolysis.
	C.c.	
Water	2·65	6·75
Bromoform	2·75	6·90
Chloroform	2·65	6·75
Hydrogen peroxide	2·50	6·27
Formic aldehyde	2·40	6·02
Salicylic acid	2·40	6·02
Thymol	2·30	5·77
Hydrocyanic acid	2·20	5·52
Iodoform	2·15	5·40
Mercuric chloride	2·15	5·40
Osmic acid	1·95	4·89
Strychnine sulphate	1·90	4·77
Toluene	1·80	4·52
Phenol	1·65	4·14
Silver nitrate	1·60	4·02
Hydrofluoric acid	0·50	1·25
Hydrochloric acid	0·40	1·00
Sodium fluoride	0·30	0·75

tried, unless it is hydrofluoric acid itself. The effect of acids in general has also been found to be very injurious.*

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JANUARY 31ST, 1901.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, February 11th, 1901.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 216 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Jan. 1st to Jan. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 216 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during January has been exceptionally small, only 1·04 inches having been registered; the average fall for the past thirty-five years is 2·08 inches; we therefore have to record a deficit of 1·04 inches, or 50·0 per cent on the thirty-five years' average.

Our bacteriological examinations of 550 samples have given the results recorded in the following table; we have also examined 40 other samples, from special standpipes, &c., making a total of 590 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 27 samples) ..	671
New River, filtered (mean of 137 samples) ..	28
Thames, unfiltered (mean of 27 samples) ..	4069
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 293 samples)	49
Ditto ditto .. .. highest	363
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 27 samples) ..	450
River Lea, from the East London Company's clear-water wells (mean of 39 samples) ..	16

Of the 469 samples of the filtered water supplied to London, examined bacteriologically during the past month, fifty-nine samples, or 12·5 per cent of the whole number of samples examined, contained more than 100 microbes per c.c.; the mean of the excess samples being 150. The microbic purity of the general supply was not so good as during the month of December; this was no doubt due to the heavy snow-fall and foggy weather experienced during the second week in January. For the last fortnight the water has been in its normal good condition for the time of year.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

* Quite recently, in fact since this article was written, Kastle and Hardin have been engaged in studying the toxic action of different acids on lipase. It is their intention to present the results obtained in the form of a separate communication. It may not be out of place to state in this connection, however, that it has been found in general that the toxic effect of acids upon lipase is proportional to their strength.

SOME PRINCIPLES AND METHODS OF ROCK ANALYSIS.*

By W. F. HILLEBRAND.

(Continued from p. 81).

II. *Specific Gravity* (continued).

Pycnometer Method.

IF the pycnometer has to be used, as is generally the case when the density of any one of the mineral ingredients of a rock is desired after separation by one of the approved methods, it being then in a more or less finely divided state, the most accurate procedure is that adopted in this laboratory by Mr. L. G. Eakins a number of years ago. The pycnometer used is one with a capillary stopper, provided with a millimetre scale etched in the glass, the divisions being numbered both ways from the centre and calibrated by mercury so that the value of each one in weight of water is known. The capacity of the flask filled with water to the zero division is then calculated for every half degree of temperature from 0° C. to 30° C., by making a series of careful weighings, in which, the capacity of the stem being known, it is quite immaterial at what level the water stands provided it is within the limits of the scale. The exact temperature is obtained by an accurate thermometer placed in a companion vessel of similar shape to the pycnometer, and containing a like amount of water, both being left in the balance case till its temperature has been nearly or quite assumed, as shown by a second thermometer. The weighing must of course be made before the thread of water has sunk beneath the lowest division, which it will do after a time, even though at first filling the bore to the top of the stopper; and the corrected weight full of water to the zero mark is found by adding or subtracting the needed amount, as shown by the height of the thread on the scale.

For each pycnometer in use, and these are of different sizes, is prepared a table showing its weight, the value of each scale division in grms. of water, and the capacity of the flask at different temperatures, as indicated above. The preparation of such a series of flasks is time saved in the end, for the weighing of the flask full of water each time a density determination is made is rendered superfluous. All that is necessary is to look up in the table the weight corresponding to the temperature.

The density of the previously weighed substance in this case is now determined in much the same way, after the unstoppered pycnometer containing it and nearly filled with water has stood with its companion vessel of water under the air-pump the necessary length of time. The water needed to fill the flask is taken from its companion.

All who have used the pycnometer method for fine substances know the difficulty experienced in preventing a portion from being held at the surface, despite all attempts at making it sink. Hence it often happens that a very small portion runs out around the sides of the stopper on inserting it. If the flask rests in a small tared dish the grains thus forced out may be washed down into it and weighed after evaporation in order to get the correct weight of that in the flask; or, after weighing, the contents of the flask may be emptied into a tared dish, and the water slowly evaporated off in order to get the weight

* *Bulletin of the United States Geological Survey*, No. 176.

of the mineral. Usually this way is less to be recommended than the other.

Heavy Solutions not Suitable for Rocks.

Because of their roughness, porosity, and complex mineral composition, the density of rock fragments can not be accurately determined by that of heavy solutions in which they may remain suspended.

III. *Preparation of Sample for Analysis.*

Quantity of Rock to be Crushed.

In the great majority of cases a few chips from a hand specimen will well represent the average of the mass, but with rocks in which a porphyritic structure is strongly developed the case is different. Here a large sample should be provided, gauged according to the size of the crystals, and the whole of this should be crushed and quartered down for the final sample. Unless this is done, it is manifest that the analysis may represent anything but the true average composition of the rock.

Crushing.

Mechanical appliances for reducing samples to fine powder are much in use in technical laboratories, where they answer their purpose more or less satisfactorily, and something similar is needed in those scientific laboratories where rock analysis is of daily occurrence, and many samples must be reduced to fine powder in a short space of time. For accurate analyses the use of steel crushers and mortars is out of the question, because of the danger of contamination by particles of metal, and the impossibility of cleansing the roughened surfaces after they have been in use a short time. Extraction by the aid of a magnet of steel particles thus introduced into the powder is quite inadmissible, since the rocks themselves, almost without exception, contain magnetic minerals. The method of rough crushing on a small scale found to be most satisfactory in practice is to place each fragment as received on a hard steel plate about 4½ c.m. thick and 10 c.m. square, on which is likewise placed a steel ring 2 c.m. high, and of about 6 c.m. inner diameter, to prevent undue flying of fragments when broken by a hardened hammer. In this way a considerable sample can soon be sufficiently reduced for transfer to the agate grinding mortar with a minimum of metallic contamination.

For breaking large pieces or rock to small sizes a thick iron plate with specially hardened surface and a similarly hardened pounder, such as street pavers use, will probably render the best service, but the hardening must be done with extreme care.

Grinding.

Of the various grinding arrangements on the market purporting to fulfil their purpose few, if any, observed have met the conditions required by the work in hand. Either the mechanical arrangement is complicated or cumbersome, requiring more power or space than is usually at disposal, or causing too much noise, or thorough cleansing is difficult and troublesome, or there is likelihood of contamination from oil or grease or lack of facility for the removal of all powder from the mortar. These last defects are especially prominent in those forms in which the mortar is fixed in its setting.

All rock samples have therefore been reduced to powder by hand, involving a great expenditure of time and labour. Ordinarily an extremely fine state of division is unnecessary, except in the case of those portions in which alkalis and ferrous iron are to be estimated, or where soluble constituents are to be removed by acids, &c., and in such cases the final grinding can be done at the balance table on a small portion slightly in excess of the quantity to be weighed off.

The process of sifting through fine cloth, the German "Beuteln," is not one always to be commended, because of the time required, and, more especially, because of the certainty of contamination by cloth fibre, which in the ferrous-iron portion might affect the result. Still less should metal sieves be used.

Weight of Ground Sample.

The sample when ground should weigh not less than 10 grms., and preferably 20 in case it should be necessary to repeat or advisable to employ unusually large portions for certain determinations, notably carbonic acid. Rock analysis has in this respect an advantage over mineral analysis, since material is almost always available in ample quantity, and any desired number of separate portions may be used, whereas with a mineral the analyst is frequently compelled to determine many or all constituents in a single, often very small, portion of the powder. This course often involves delay, and the employment of more complicated methods of separation than are usually necessary in rock analysis.

IV. *Water—Hygroscopic, Zeolitic, Crystal.*

Importance of Employing Air-dry Powder for Analysis.—The time-honoured custom of drying a powdered specimen before bottling and weighing has long seemed to the writer one that has no sound basis in reason. Its object is of course plain, namely, that of securing a uniform hygroscopic condition as a basis for convenient comparison of analytical results, since some rocks contain more hygroscopic moisture than others. Nothing, however, is more certain than that by the time the substance is weighed it has re-absorbed a certain amount of moisture, small, indeed, in most cases, but very appreciable in others; and further, with every opening of the tube moisture-laden air enters and is enclosed with the remainder of the dry powder. It therefore may very well happen that a powder at first dry will, after several openings of the tube, especially at considerable intervals, be nearly as moist as when first inclosed.

It is preferable to weigh the air-dry powder and to make a special determination of moisture. If all the portions necessary for an analysis are weighed out one after another, or even at different times on the same day, the error due to difference of hygroscopicity in dry and moist weather, which for most of the separate portions is an entirely negligible quantity, is eliminated. Only in the main portion, in which silica and the majority of the bases are to be estimated, can it ever be an appreciable factor.

Temperature of Drying.—As to the temperature to be adopted for drying in order to determine so-called hygroscopic moisture, the practice has varied at different times and with different workers, ranging from 100° to 110° C. For the great majority of rock specimens it is quite immaterial which of these temperatures is adopted, since no greater loss is experienced at the higher than at the lower temperature, given a sufficient time for the latter. It is the present practice in this laboratory to employ a toluene bath giving a temperature of about 105° C. Should the results show a very unusually high loss, the powder is reheated at, say, 125°, in order to learn if the loss is progressive with increased temperature. In the affirmative case it may be well to repeat the drying at 100°, for a portion of the loss at 105° was probably due to combined water from a mineral or minerals in the rock; but in that case even the loss at 100° may sometimes very well include combined water, in which case drying over sulphuric acid alone may be desirable, or over dry sand.

Cautionary Hints.—In this latter connection it is proper to point out certain pitfalls in the path of the unwary, which, however, are far more likely to be encountered in the analysis of minerals, where their influence may be of far-reaching consequence.

A mineral which loses a great deal of water over sulphuric acid—2 or 3 per cent, for instance—may need an exposure of several days or even weeks for its complete extraction. If the weighings are made from day to day, the apparent limit may be reached long before all water really removable has been taken up by the acid. Whenever the crucible, after weighing, is replaced in the

desiccator it is no longer in a dry but a more or less moist atmosphere, and its contents, even when covered, sometimes absorb a part of this moisture, and retain it so persistently that the acid is unable to bring the powder beyond its previous state of dryness in the next twenty-four hours. In fact, it may be unable even to reach it unless greater time is allowed. An experiment on 1 grm. of tyrolite, made and published some years ago, seems to illustrate this point in part:—

TABLE III.

Hours exposed.	Loss. Grm.	Hours exposed.	Loss. Grm.
18	0·0231	24	0·0002
26	0·0083	24	0·0003
23	0·0029	48	0·0006
24	0·0012	24	0·0002
23	0·0008		
24	0·0001	283	0·0380
25	0·0003		

placed, and again weighed the next day. It had regained 1½ per cent of its original weight, although the desiccator was tightly closed and the crucible covered, showing apparently a drying power superior to that of the acid.

A specimen of tyrolite was found on one occasion to lose 10·34 per cent at 280° C., and on another occasion 14·33 per cent. In the latter case the drying and heating at progressive temperatures had continued during a period of 528 hours, the weighings being made usually from day to day; whereas in the former the duration of the experiment was much shorter, and the intervals between weighings were but a few hours each.

Procedure in Special Cases.—For experiments of the kind just indicated the powder should be heated in a weighed tube, through which a current of dry air can be passed, and allowed to cool therein, or else the water given off should be collected and directly weighed in suitable absorption tubes, even though the long time often required is an objection to this latter method, since the absorption tube may gain weight, other than that of the

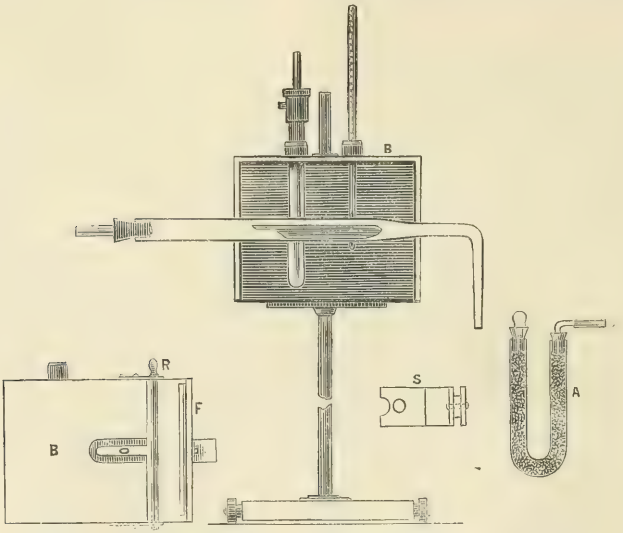

FIG. 3.—CHATARD'S FORM OF DRYING-OVEN FOR WATER DETERMINATIONS.

B, Copper box, 18 c.m. long, 10½ c.m. high, 9 c.m. wide, open in front, its sides and top covered with asbestos board; S, two slides of different sizes to close the openings, O, after the tube is in position; F, asbestos board front, stiffened by an interlaid sheet of copper; R, metal rod to hold front in place; A, calcium chloride absorption tube.

The experiment might reasonably have been considered ended after the one hundred and fifty-eighth hour, when a loss of but 0·1 milligrm. was shown during twenty-four hours; but nevertheless a nearly steady loss of 0·3 milligrm. per day took place for six days more, and might have been longer observed but for the interruption of the experiment.

Again, it is a common practice to determine the water given off by hydrous minerals in an air-bath at temperatures far above 100° C. To insure accuracy this experiment should not be made in crucibles or dishes which must be cooled in a desiccator. One instance will suffice: A grm. of a mineral mixture containing about 17 per cent of water, of which about 3 per cent was driven off at 100° and 8 or 9 per cent at 280°, was, after several hours' heating at the latter temperature, placed in a desiccator over sulphuric acid, and weighed as soon as cold, then re-

water from the mineral, sufficient to introduce an appreciable error.

The recent important research of Friedel (*Bull. Soc. Min.*, 1896, vol. xix., pp. 14, 94; *Comptes Rendus*, 1896, vol. cxxii., p. 1006), well shows what errors are possible in the determination of this easily removable water, since he found that certain zeolites which had been largely dehydrated but not heated to the point of rupture of the molecular net, could then absorb, instead of water, various dry gases in which they might be placed, as carbon dioxide, ammonia, carbon disulphide, and others, even air in large quantities, and certain liquids. In the light of this observation the cause of the great increase of 1½ per cent in weight of the partially dehydrated mineral mentioned above may very possibly be attributed to air from the desiccator instead of moisture, as was at the time supposed. At any rate, as Friedel says, the danger of

accepting a loss in weight as an index of the amount of water lost is clearly shown, and thus that method of determining water is for many cases fully discredited. Just what method to adopt must be largely left to the judgment of the operator, who will often be guided by the mineral composition of the rock as revealed by the unaided eye or the microscope.

Friedel (*loc. cit.*) indicates a means for determining the true weight of water lost by minerals behaving like the zeolites, even without collecting the water lost, namely, by driving out of the dehydrated and weighed mineral, under proper precautions, any air it may have absorbed in the process of drying and cooling, and collecting and measuring this air, and thus finding its weight, which, added to the apparent loss, gives the true contents in water.

Argument in Favour of including Hygroscopic Water in Summation.—The question has been asked: "If the so-called hygroscopic water is not always such, but not infrequently includes combined water, why is not its determination and separate entry in the analysis entirely unnecessary? Why make a distinction, which, after all, may not be a true one?" The question involves the further consideration of the advisability of including in the analysis at all the loss at 100° or 110° C. Many petrographers desire to have all analyses referred to a moisture-free basis, in order that they shall be strictly comparable, and therefore, would omit the "hygroscopic" water from the list of constituents. This would be eminently proper were it always possible to be sure that the loss at 100° truly represents mechanically held water. Since it very often represents more, and the determination as to whether or not it does in each case is not always possible, and would add to the time required for the analysis, it seems necessary to include this water. What errors may arise from its exclusion the following rather extreme case well illustrates: Certain rocks of Wyoming in powder form lost from 1 to 2 per cent of moisture at 110°. That not even an appreciable fraction of this was truly hygroscopic, the fact of the uncrushed rocks losing the same amount fully demonstrates; yet the rule followed by many chemists and petrographers would have involved the removal of all this water as a preliminary to beginning the analysis, and not only would a most important characteristic have passed unnoticed, but the analyst would have reported an incorrect analysis, inviting to false conclusions and possibly serious confusion.

Separate Entry of Hygroscopic and Combined Water.—To revert now to the primary question, it may be said that the estimation of the loss at 100° or 110° C. and its separate entry in the analysis is advisable as not infrequently affording at once to the lithologist an indication of the mineral character of one or more of the rock constituents, thus perhaps confirming the microscopical evidence or suggesting further examination in that line. An unusually high loss at 100° would be regarded as probable evidence of the presence of zeolites or other minerals carrying loosely combined water. It has been objected that the true hygroscopic moisture varies with the degree of comminution of the sample and with the condition of the air at the time of weighing, and that it is therefore improper to incorporate it in the analysis; but this variation is ordinarily not at all great. Perhaps the time may come when it will be the rule to ascertain by additional heating at a higher temperature whether the water lost at 100° is to be regarded as purely hygroscopic. In such case it would be proper to omit it, and a distinct advance would undoubtedly be scored.

Is all True Hygroscopic Water Expelled at 100°?—It has been tacitly assumed in the foregoing that true hygroscopic water can all be expelled at 100°, which perhaps is not to be accepted as universally true. Eminent authority holds that it is impossible, in the cases of certain foliaceous minerals, notably the micas, to thus entirely remove it, but that a part is only driven off at higher temperatures. If this is true a further uncertainty is introduced in its determination, which not only strengthens the argument in favour of entering all water in the tabulation, but also serves to emphasise the difficulties of the situation.

Apparatus for the Direct Determination of Water at Different Temperatures.

A form of drying-oven devised by Dr. T. M. Chatard (*Am. Chem. Journ.*, 1891, vol. xiii., p. 110; *Bull. U. S. Geol. Survey*, No. 78, p. 84) is in use in this laboratory for determining water at different temperatures up to 350° C., and gives entire satisfaction. It is an asbestos-covered copper box, B, shown in different aspects and parts in the accompanying Fig. 3. The box is so constructed that the tube with its contents can be removed without detaching from either the drying or collecting tubes, which is a great advantage if it is desired to afterwards apply the direct heat of a lamp in order to expel the water retained at 300° to 350° C. To facilitate this removal the stand is on rollers, so that after clamping the projecting end of the tube and removing the front of the box, F, and the little side pieces, S, closing the horizontal slits, the oven can be rolled bodily backward, leaving the tube and its attachments in their original position, ready for further heating over a burner or blast. The removable front, F, of the oven is made of two pieces of sheet asbestos board stiffened by an interlaid piece of sheet copper. The inner piece of asbestos board fits snugly into the box, while the outer one, being slightly larger, by its projecting edges hinders the door from falling in and helps to prevent air currents. This door is held in place by the metal rod R. The little slides, S, are made in a somewhat similar manner, and are intended to slip in from the front and close the two openings, O, after the tube is in place, but before closing the front.

For other forms of tubes adapted to similar determinations, see Figs. 6, 10, and 11.

(To be continued).

Institute of Chemistry Examinations.—Pass Lists (January, 1901).—*Intermediate Examination*: J. Evans, King's Coll., London, and Pharmaceutical Society; R. S. Finlow, Univ. Coll. of N. Wales, Bangor; E. Hinks, King's Coll., London; W. A. Handcock, Finsbury Tech. Coll., London; D. Northall-Laurie, King's Coll., London, and under E. Jackson, Esq., F.I.C.; G. Steedman, Glasgow and West of Scot. Tech. Coll. *Final A.I.C. Examination—Branch* "A" (*Mineral Chemistry*): J. H. Austin, Birmingham University; R. M. Clarke, B.Sc. (Glasgow), Glasgow University; J. W. Cotterill, Birmingham University (for Fellowship); F. Cunliffe, Owens Coll., Manchester; W. D. Dick, King's Coll., London; A. Gray, Glasgow and West of Scot. Tech. Coll.; W. Lowson, Yorkshire Coll., Leeds; A. J. Robertson, Univ. Coll., Dundee, and under R. R. Tatlock, Esq., F.I.C. *Branch* "B" (*Metallurgical Chemistry*): W. Bowen, Birmingham University. *Branch* "D" (*Organic Chemistry*): R. J. Carter, B.A. (Oxon.), Oxford University; A. T. Etheridge, B.Sc. (Lond.), Birmingham University; J. A. Lloyd, Birmingham University; J. Rogers, Glasgow and West of Scot. Tech. Coll.; W. H. Taylor, Finsbury Tech. Coll., London. *Branch* "E" (*Analysis of Food and Drugs, not including Examination in Therapeutics, Pharmacology, and Microscopy*): H. G. Bayly, King's Coll., London; E. J. Denney, A.C.G.I., Central Tech. Coll., London, and under F. Sutton, Esq., F.I.C; H. D. Hewitt, Finsbury Tech. Coll., London, and under A. C. Chapman, Esq., F.I.C.; J. H. Johnstone, B.Sc. (Vict.), Owens Coll., Manchester. *Branch* "E" (*Analysis of Food and Drugs, including an Examination in Therapeutics, Pharmacology, and Microscopy*): E. M. Chapman, Pharmaceutical Society and King's Coll., London; J. A. Dewhirst, Yorkshire Coll., Leeds, and Pharmaceutical Society; A. H. Mitchell, B.Sc. (Lond.), Owens Coll., Manchester, and Univ. Coll., London (for Fellowship); E. A. Pinchin, B.Sc.(Lond.), Roy. Coll. of Science, London.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 7th, 1901.

Professor Thorpe, C.B., F.R.S., President, in the Chair.

Messrs. R. M. Caven and J. B. Harrison were formally admitted Fellows of the Society.

The following certificates were read for the first time:—William Carrick Anderson, 2, Florentine Gardens, Hillhead, Glasgow; George Stanfield Blake, Purley Lodge, Purley, near Croydon; Edward Richards Bolton, 7, Leazes Terrace, Newcastle-on-Tyne; William Carter, 7, Victoria Street, Clitheroe; Henry Drysdale Dakin, 9, Beech Grove Terrace, Leeds; John Hanley, 4, Guion Road, Litherland, Liverpool; John Ansted Harrison, 47, London Road, Neath, Glamorganshire; Henry Herbert Higgs, 26, Anglesey Street, Lozells, Birmingham; Albert John Murphy, Preston House, Leeds; Arthur Theodore Neil, 21, South Grove, Highgate, N.; William Robertson, 41, Rosenau Road, Battersea Park, S.W.; Samuel Fenton Stell, 20, Henry Street, Keighley; George Edward Welch, 88, Caledonian Road, Leeds; Adam Storer Wylie, 93, Manchester Street, Oldham.

The Address to the King.

The President read the following Address, which the Council that afternoon had resolved to present to his Majesty the King. He moved that the Fellows of the Society should join with the Council in paying respect to the memory of the illustrious Queen they had so recently lost and in offering their homage to the new Sovereign. This was seconded by the Treasurer and carried unanimously, the Fellows all standing.

To His Most Gracious Majesty King Edward VII.

May it please your Majesty.

We, the President, Council, and Fellows of the Chemical Society, beg leave to approach your Majesty with expressions of deep sympathy in the grievous loss which your Majesty and the Empire have sustained through the death of our revered Sovereign, Queen Victoria, during whose beneficent reign the science of Chemistry, for the promotion of which her Majesty granted the Society a Royal Charter, has made immense progress.

We recall with gratitude the leading part which your illustrious Father, the Prince Consort, took in securing the extension of scientific knowledge in this country, and especially the great assistance he rendered in the foundation, in the year 1845, of the Royal College of Chemistry (since developed into the Royal College of Science), of which College he became the President.

We desire respectfully to congratulate your Majesty on your accession to the Throne, and most heartily to wish your Majesty a long, happy, and prosperous reign.

We venture to express the hope that your reign may be marked by discoveries in the science we represent not less brilliant than those which have characterised the reign of her late Majesty.

Signed on behalf of the Chemical Society,

T. E. Thorpe, President.
W. A. Tilden, Treasurer.
Wyndham R. Dunstan, Alexander Scott, } Honorary Secretaries.
R. Meldola, Foreign Secretary.

The Day and Hour of Meeting.

Mr. F. J. Lloyd asked whether the President could give any information as to the reasons which had led the Council to issue its recent circular requesting the views of the Fellows on a proposal to change the day and hour of the Ordinary Meetings of the Society.

The President, in reply, said that he was glad to take advantage of the opportunity which Mr. Lloyd had afforded him to state the attitude of the Council on the question. The expediency of an alteration in the day and hour of meeting had been mooted on more than one occasion, though no action was taken till the question was formally raised at a recent meeting of Council. The Secretaries were thereupon directed to issue with the "Journal" for this month the circular and card referred to, with the view of eliciting the opinion of the Fellows upon the subject.

With respect to Mr. Lloyd's question as to the reasons for the inquiry, he might remind the Fellows that a great change had come over the social life of London during the fifty or sixty years of the Society's existence. A great number of what used to be called the "resident" Fellows now lived in suburbs which were extending in all directions more and more widely. Moreover, the facilities for reaching town had been so enormously increased that it seemed worth while inquiring whether a re-arrangement of the day and hour of meeting would render it possible for the country Fellows to attend the meetings of the Society in greater numbers than at present. He (the President) thought it would thus be seen that the Council had good *primâ facie* grounds for testing the opinion of the general body of Fellows.

He might add that more than half of the cards issued had been returned, and of these a very large majority were in favour of the suggested alteration. No exact analysis had as yet been made, but the Fellows might be interested to know that those in favour of the change were in the ratio of about four or five to one. Of the "resident" Fellows about two to two and a-half to one were in its favour. He expressed a wish that the remaining cards should be returned as quickly as possible so that the Council might have the opportunity of considering the replies, and of dealing with the matter, if necessary, at the Annual General Meeting.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—

Andrew Charles Aitken, Thomas Stewart Barrie, John Cardew Bedwell, B.Sc., Herbert John Bult, Merrick W. Burrows, M.Sc., Robert Waley Cohen, B.A., Herbert H. Cousins, M.A., Gilbert Howard Daniel, B.Sc., Robert Dodd, Frederick G. Donnan, M.A., Ph.D., John Alfred Emery, Reginald W. Ferguson, Henry Edward Haddon, Arthur Houldershaw, Bernard Farmborough Howard, Edward Hughes, Robert Salmon Hutton, M.Sc., Stephen Archigenes Ionides, Major J. L. T. Jones, I.M.S., Robert Henry Jones, M.Sc., H. T. G. van der Linde, Nicholas Henry Martin, James Menzies, William Meredith, James Moir, M.A., B.Sc., Arthur W. Nunn, Theodore Henry Page, Thomas Slater Price, Ph.D., D.Sc., Lionel Guy Radcliffe, William Cecil Ramsden, Herbert Kilburn Scott, Harry Metcalfe Smith, John Talbot, B.A., B.Sc., Albert Edward Thomas, B.Sc., Major-General J. Waterhouse, William A. Wayland, J. S. Wilson, M.D., C.M.

Of the following papers, those marked * were read:—

*8. "*The Action of Hydrogen Bromide on Carbohydrates.*" By H. J. H. Fenton and Mildred Gostling.

It was previously shown by the authors (*Trans.*, 1898, lxxiii., 554, and 1899, lxxv., 423), that bromomethylfurfuraldehyde results when hydrogen bromide acts upon lævulose, sorbose, inulin, or cane sugar, and it was shown that the formation of this substance is characteristic of ketohexoses or of substances which give rise to them on hydrolysis. The experiments have now been extended, using a higher temperature and chloroform as the solvent. Under these conditions, all forms of *cellulose* give large yields of bromomethylfurfuraldehyde, and the results appear conclusively to prove that cellulose must contain a grouping or nucleus similar to that in lævulose. An account was also given of the behaviour of several other carbohydrates under similar conditions.

*9. "*The Ketonic Constitution of Cellulose.*" By C. F. Cross and E. J. Bevan.

Having received a private communication of the results obtained by Fenton and Gostling, which are described in the preceding note, it has been deemed opportune to state fully the experimental evidence available for the solution of the problem of the constitution of cellulose.

For the view that cellulose is a near analogue of starch, that is, a polyanhydride of dextrose, the evidence is slender, resting mainly (1) on the well established empirical formula $(C_6H_{10}O_5)_n$ and (2) on the somewhat superficial study of the products of ultimate hydrolysis by Braconnot (*Ann.*, 1819, [ii.], xii., 172), and Flechsig (*Zeit. Physiol. Chem.*, 1883, vii., 523).

The later evidence comprises the following items: (*a*) The tetracetate (Cross and Bevan) appears to be an ester of the unresolved cellulose (anhydride) with a formula $C_6H_8O\cdot(OAc)_4$, from which may be deduced as probable the ketonic formula $CO{:}(CHOH)_4{:}CH_2$, for the cellulose unit; (*b*) Will and Lenze have shown (*Ber.*, 1898, xxxi., 68) that the ketoses yield nitric esters with two ester groups less than the corresponding aldoses, two hydroxyl groups being condensed by internal reaction. Cellulose giving a trinitrate (C_6) with yields less than the theoretical (for the simple ester reaction) conforms with this general character of the ketoses and their anhydrides; (*c*) Faber and Tollens (*Ber.*, 1899, xxxii., 2595), in a recent study of the oxycelluloses, have identified in the soluble products of the oxidation tartaric and oxalic acids and a dibasic acid containing five atoms of carbon. *Saccharic acid was not formed.* Further, the oxycelluloses digested with calcium hydroxide yield dioxybutyric and isosaccharic acids. Acids with the normal six carbon chain are again conspicuously absent; (*d*) Brown and Morris (*Trans.*, 1893, lxiii., 604) have established that cane sugar is a first product of chlorophyllic assimilation, and starch is probably only a derived overflow product. Further, that cane-sugar, amongst the soluble carbohydrates, has a maximum nutritive value when tested in relation to chlorophyllic assimilation (*Trans.*, 1890, lxxvii., 484). A similar observation, but more directly with lævulose in relation to cellulose production, was made by A. Brown (*Trans.*, 1886, xlix., 432).

On the above grounds, the authors had previously concluded that cellulose is not a polyaldose (anhydride), but is of ketonic constitution.

Fenton and Gostling, by condensing celluloses to methylfurfural as a main reaction, have opened an entirely new direction of experimental attack, the first result of which is at least to render the polyaldose view of its constitution questionable.

Their results directly suggest that lævulose or other ketose is the raw material for cellulose elaboration, and also offer a simple explanation of the origin of unsaturated compounds such as the furfural derivatives which are constituents of the lignone complex. It also further weakens the evidence upon which all furfural yielding constituents of plants have been assumed to be pentoses or pentosanes.

Discussion.

Dr. Horace Brown, whilst fully admitting that a considerable amount of evidence can now be brought forward in favour of the ketonic constitution of cellulose, expressed a doubt whether the small amounts of the bromo-derivative of methylfurfural obtained by Mr. Fenton from purified starches would justify the conclusion that starch contains the carbonyl group. More evidence is required of the specific nature of the reaction, and also of the absolute freedom of the starch from traces of "starch cellulose." He was unable to add anything to the physiological evidence put forward by Dr. Morris and himself some years ago, and which certainly did appear to lend some countenance to the view that in the plant economy lævulose has some genetic connection with cellulose rather than with starch.

Mr. Fenton said that although he and his colleague were at present concerned chiefly in demonstrating a ketonic grouping or nucleus in cellulose, he considered it not at all improbable that such a grouping exists, as a fraction of the whole, in the complex molecule of starch.

The product of hydrolysis of the portion containing such a grouping may very conceivably have been overlooked in the methods of identification hitherto employed.

*10. "*Note on a Method for Comparing the Affinity Values of Acids.*" By H. J. H. Fenton and H. O. Jones.

In a former communication (*Trans.*, 1901, lxxix., 92), the authors described a simple method for comparing the affinity values of acids based upon the decompositions of the hydrazone of oxalacetic acid. This substance when heated with pure water yields the hydrazone of pyruvic acid and carbon dioxide:—

$$\begin{array}{l} CH_2CO_2H \\ | \\ C{:}N_2HPh \\ | \\ CO_2H \end{array} = \begin{array}{l} CH_3 \\ | \\ C{:}N_2HPh \\ | \\ CO_2H \end{array} + CO_2.$$

From 83 to 90 per cent is decomposed in this manner, the slight differences observed in different specimens depending on their purity. But in presence of acids of sufficient concentration an entirely different change occurs; water is lost and Wislicenus's pyrazolone carboxylic acid is formed without evolution of any carbon dioxide:—

$$\begin{array}{l} CH_2CO\cdot OH \\ | \\ C{:}N\cdot N\overset{H}{\underset{Ph}{}} \\ | \\ CO_2H \end{array} = \begin{array}{l} CH_2\cdot CO \\ | \quad | \\ C:N\cdot NPh \\ | \\ CO_2H \end{array} + H_2O.$$

With acids of insufficient concentration both changes occur simultaneously, the amount of carbon dioxide evolved being less as the concentration of the acid increases. Making exactly parallel experiments with different acids, it was shown that the volumes of carbon dioxide obtained are in the inverse order of the affinity-values of the acids.

In order to explain the nature of this influence, the authors suggest that the undissociated molecule of the hydrazone tends only to lose water, giving the pyrazolone derivative, but that the negative ion, $CO_2H—CN_2HPh—CH_2CO_2$, is unstable and tends to lose carbon dioxide. Upon this hypothesis any circumstance tending to prevent ionisation should favour the production of the pyrazolone derivative, and the presence therefore of a sufficient concentration of hydrogen ions should cause the change to take place in this direction more or less completely.

Other explanations might, of course, be offered, referring, for example, to the dehydrating influence of acids or to the "basic" character of the pyrazolone ring, and it was therefore considered advisable to make further experiments in order to ascertain whether other conditions went in harmony with the ionisation hypothesis.

The investigations had reference to the influence of—(*a*) salts, (*b*) non-electrolytes, (*c*) acids in presence of their own salts, and (*d*) solvents other than water.

In all the experiments the conditions were made exactly parallel, about 0·1 grm. of the hydrazone being heated to 100° with 7·5 c.c. of the liquid to be examined in the manner previously described.

The solutions examined and results obtained are given in the accompanying table.

Bases likewise have practically no influence; thus 0·1001 grm. hydrazone heated with a quantity of soda representing slightly *less* than 1 equivalent gave 8·58 c.c. (corr.) of carbon dioxide.

The conclusions which may be drawn from these experiments are:—

(*a*) The influence of salts, bases, and non-electrolytes is *nil*, the results being practically identical with that given by pure water;

	Weight in grms. in 100 c.c.	Weight of hydrazone.	Corrected volume of carbon dioxide.
			C.c.
1. Pure water	—	0·0998	8·31
2. Sodium sulphate (cryst.).	6	0·1000	8·75
3. Cane-sugar	6	0·1005	8·12
4. Urea..	1	0·1000	8·31
5. Sulphuric acid	0·49	0·1003	2·60
6. Sulphuric acid and sodium sulphate	0·49 / 6	0·1000	7·12
7. Acetic acid	0·6	0·1001	7·07
8. Acetic acid and sodium acetate (cryst.)	0·6 / 3	0·1002	8·31
9. Amyl alcohol	—	0·0989	3·53
10. Toluene	—	0·1078	2·29
11. Nitrobenzene	—	0·1026	2·29

(*b*) The effect of a salt in presence of its own acid is greatly to diminish the influence of the acid; and

(*c*) Solvents having different ionising powers give very different results; the amount of carbon dioxide evolved being greatest in the case of water, less in amyl alcohol, and least in toluene and nitrobenzene.

With regard to the three last-named solvents, it may be remarked that, although they were carefully dried, water is produced in the pyrazolone formation; hence it is not surprising that some action should take place in a solvent such as toluene, which when pure has presumably little or no ionising power.

It is evident therefore that the results are, on the whole, well in harmony with the ionisation hypothesis, which certainly appears to offer the most satisfactory explanation of the phenomena, although other explanations are, of course, possible.

The purification of the hydrazone by re-crystallisation is a troublesome and wasteful process, but the crude substance answers perfectly, since the results required are only relative. It is advisable to employ the same sample, for each set of observations, and the substance should be freshly prepared.

Discussion.

Dr. Travers remarked that the evolution of carbon dioxide from the acid seemed to take place under conditions similar to those which obtained during the electrolysis of the salt of an acid, and to be dependent on the concentration of the negative ion, in one case in the solution generally, and in the other on the surface of the anode. It would be interesting to know how the corresponding diphenylhydrazone would behave under similar conditions.

Mr. Fenton, in reply, said that one example of a disubstituted hydrazine had been investigated, namely, benzylphenylhydrazine, but that the oxalacetic derivative was extremely unstable, and only the pyruvic derivative could be isolated.

(To be continued).

Royal Institution.—On Saturday next, February 23, the Right Hon. Lord Rayleigh, Professor of Natural Philosophy in the Royal Institution, will deliver the first of a course of six lectures at the Royal Institution on "Sound and Vibrations." On Tuesday, February 26, Dr. Allan Macfadyen will begin a course of five lectures on "The Cell as the Unit of Life"; and on Thursday, February 28, Professor Percy Gardner will deliver the first of a course of three lectures on "Greek and Roman Portrait Sculpture."

NOTICES OF BOOKS.

On Sanitary and Other Matters. By George S. Keith, M.D., LL.D., &c. London: Adam and Charles Black. 1900. Pp. 127.

The papers comprising this volume are of a curiously mixed character, and we cannot see that they lead to anything in particular. The author is a firm believer in earth closets as a preventive of the waste of water; there is of course no objection to their use by intelligent persons, but we shudder to think what the result would be if their general use was ordained throughout London.

Another chapter, "The Story of an Eye," is purely a personal narrative, and though it compels our sympathy for the author's sufferings, it is really only of interest to members of the medical profession.

Altogether we cannot help feeling after a perusal of this book that the author is "oppositely polarised" to the greater number of his fellow creatures.

The Microscopy of the More Commonly Occurring Starches. By Hugh Galt, M.B., C.M. (Honours, Glasgow), D.P.H. (Camb.), &c. Illustrated by twenty-two original Micro-photographs. London: Baillière, Tindall, and Cox. 1900. Pp. 108.

The results of an investigation carried out by the author as a research student in the Public Health Laboratory at the University of Glasgow are embodied in this work.

It is pointed out by the author that in spite of the importance from many points of view of an accurate delineation of the starches, very little has been done in this direction, in this country, up to the present time; moreover, a good deal of the information given by the various text-books is not remarkable for accuracy.

A large portion of the work on this subject has naturally to be done by the aid of the microscope, and to render this work intelligible to others either diagrams or photographs must be made; a good deal of stress is here laid on the "personal equation" of the individual, whether teacher or student, who makes the diagrams. This drawback is almost entirely avoided by adopting microphotographic methods; there is, however, still the risk of the photograph not telling the whole truth.

The author then fully describes and illustrates a number of different kinds of starches, and sums up their leading microscopical characters in two tables on pp. 101—102. The book is well arranged and printed, and fully indexed.

The Boyle System of Ventilation. Robert Boyle and Sons, Limited.

This handsome volume may be best described as a treatise on Ventilation combined with a Trade Catalogue.

The particular system applied by the authors consists in removing the pressure of the external air from the top of the shaft by means of an "air-pump" ventilator, combined with certain improved air inlets at the lower parts of the building, thus causing a continuous change of air at low velocity in accordance with the natural laws which govern ventilation.

The higher temperature in an occupied building, particularly in cold weather, combined with the ascensional movement of the heated air arising from the lungs and body, are also utilised as auxiliaries in changing the air even when there is no perceptible movement outside. It is stated that the special construction of the air inlets completely prevents the lodging or accumulation of dust, and they are also easily accessible for cleaning purposes. In the last few pages there is an interesting series of coloured diagrams, illustrating several systems of ventilation, both good and bad. We need hardly add that the Boyle system is shown to be the best.

CORRESPONDENCE.

NUMBERING CRUCIBLES.

To the Editor of the Chemical News.

Sir,—It would be a great convenience if manufacturers would mark porcelain crucibles with consecutive numbers—in sets, say, of five or ten. Where several estimations are in hand simultaneously, crucibles not infrequently get mixed in the exsiccator unless some distinguishing mark has been affixed.

The numbers would preferably be on the side, but if this were objectionable from any manufacturing point of view, it could very well be on the biscuit surface at the bottom along with the trade mark. Failing this, however, numbers can be marked on the bottoms with a 10 per cent solution of platinic chloride containing a little gum acacia, applied, of course, with a quill, allow to dry, and heat up the crucible in a blowpipe flame. The results are very distinct.—I am, &c.,

A. Andrew Kelly.

41, Highfield Road, Dartford,
February 8, 1901.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxii., No. 4, January 28, 1901.

Hydrogen from Igneous Rocks. Action of Water-vapour on Ferrous Salts.—Armand Gautier.—In a preceding paper the author showed that igneous rocks, when brought to a red heat, evolve a considerable quantity of gas which, for the most part, did not pre-exist. He now further examines these evolved gases and the processes which cause their presence. In all cases hydrogen is present in the largest proportion, but this gas is always accompanied by a little ammonia. The various rocks, when powdered and acted upon by acidulated water, show the presence of small quantities of ferrous salts. The explanation, apparently, is that when ferrous salts (chloride, sulphide, carbonate, &c.) are heated to 750° or 800° in the presence of water-vapour, the negative radicle is volatile at this temperature, and incapable of yielding up its oxygen, so an oxide of iron is always formed—generally the magnetic oxide—at the same time as the free hydrogen.

Nitrate of Uranium.—Œchsner de Coninck.—An examination of the action of heat on uranium nitrate leads the author to the following conclusions:—(1) Calcination of crystalline uranium nitrate gives a red modification of the sesquioxide of uranium, which is apparently the polymer of the orange modification. (2) This red modification, calcined for about forty hours at a dull red heat in a platinum capsule, is partially transformed into a brown oxide. If heated for the same length of time at a bright red heat in a closed platinum crucible, it is not transformed into the green oxide, but a very small quantity of brown oxide is produced. (3) The orange modification of uranium sesquioxide, which is produced when uranium nitrate is but slightly heated, if kept at a dull red heat for twenty-six hours is partially transformed into the red variety.

Action of Boron Bromide on the Iodides of Phosphorus and on the Halogen Compounds of Arsenic and Antimony.—M. Tarible.—The author's researches on the action of boron bromide on the halogen compounds of phosphorus, arsenic, and antimony, lead to the results which are shown in the following table:—

Body placed in presence of BBr_3.	Products of the reaction.
PCl_3	The compound $PCl_3.2BBr_3$
PCl_5	,, $PCl_5.2BBr_3$
PBr_3	,, $PBr_3.BBr_3$
PBr_5	,, $PBr_5.BBr_3$
P_2I_4	,, $P_2I_4.2BBr_3$
PI_3	,, $P_2I_4.2BBr_3 + I$
$AsCl_3$	Double decomposition.
$AsBr_3$, AsI_3, AsI_5	Solution.
$SbCl_3$	Double decomposition.
$SbCl_5$	,, ,,
$SbBr_3$	Solution.
SbI_3	,,

All these reactions are in complete harmony with the thermo-chemical constants determined by different observers.

Action of Œnanthylic Alcohol on its Sodium Derivative. New Method of Synthesis of Alcohols. Marcel Guerbet.—When œnanthylic alcohol acts on its sodium derivative, the following substances are formed:—Œnanthylic acid, di-œnanthylic alcohol, tri-œnanthylic alcohol, and the corresponding acid. The tri-œnanthylic alcohol is due presumably to the ulterior action of the di-œnanthylic alcohol already formed on the sodium derivative of œnanthylic alcohol still present in the mixture:—$2C_{14}H_{30}O + C_7H_{15}NaO = C_{21}H_{44}O + C_{14}H_{27}NaO_2 + 4H$. These reactions are in every way analogous to those previously observed with inactive amylic alcohol; that reaction, in particular, which gives rise to tricœnanthylic alcohol shows that it is possible to generalise, at least with regard to the alcohols higher than butylic alcohol, and to state that when a primary alcohol is heated with the sodium derivative of another primary alcohol the following reaction takes place:—

$$2C_mH_{2m+2}O + C_nH_{2n+1}NaO = C_{m+n}H_{2(m+n)+2}O + C_mH_{2m-1}NaO_2 + 4H.$$

Direct Hydrogenation in presence of Reduced Nickel. Preparation of Hexahydrobenzene.—Paul Sabatier and J. B. Senderens.—Reduced nickel is a very active agent, causing hydrogenations and molecular decompositions to take place at a comparatively low temperature. The action of the metal is certainly due to the formation of temporary products, such as unstable hydrides. These products provoke a large number of exothermic reactions which only take place usually at high temperatures, and which are unfavourable for the stability of the substance produced. This process permits of the direct hydrogenation of benzene and its homologues at temperatures below 300°. Hexahydrobenzene is thus formed in an almost pure state:—$C_6H_6 + H_6 = C_6H_{12}$.

MEETINGS FOR THE WEEK.

Monday, 25th.—Society of Arts, 8. (Cantor Lectures). "The Bearings of Geometry on the Chemistry of Fermentation," by W. J. Pope.
—— Royal Institution, 3. "Practical Mechanics" (Experimentally treated), by Prof. J. A. Ewing, M.A., F.R.S., M.Inst.C.E.

Tuesday, 26th.—Royal Institution, 3. "The Cell as the Unit of Life," by Allan Macfadyen, M.D., B.Sc.

Wednesday, 27th.—Society of Arts, 8. "The Outlook for the World's Timber Supply," by Dr. W. Schlich, C.I.E.

Thursday, 28th.—Society of Arts, 4.30 (at the Imperial Institute, South Kensington). "Railways and Famine," by Horace Bell, M.Inst.C.E.
—— Royal Institution, 3. "Greek and Roman Portrait Sculpture," by Prof. Percy Gardner, Litt.D.

Friday, March 1st.—Royal Institution, 9. "Enamels," by Henry Hardinge Cunynghame, C.B., M.A.

Saturday, 2nd.—Royal Institution, 3. "Sound and Vibrations," by the Rt. Hon. Lord Rayleigh, F.R.S., &c.

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THE CHEMICAL NEWS.

Vol. LXXXIII., No. 2153.

THE BOILING-POINT OF LIQUID HYDROGEN, DETERMINED BY HYDROGEN AND HELIUM GAS THERMOMETERS.*

By JAMES DEWAR, M.A., LL.D.,
Professor of Chemistry at the Royal Institution, and Jacksonian Professor, University of Cambridge.

In a former paper ("On the Boiling-point of Liquid Hydrogen under Reduced Pressure," *Roy. Soc. Proc.*, 1898), it was shown that a platinum-resistance thermometer gave for the boiling-point of hydrogen −238·4° C., or 34·6° absolute. As this value depended on an empirical law correlating temperature and resistance which might break down at such an exceptional temperature, and was in any case deduced by a large extrapolation, it became necessary to have recourse to the gas thermometer.

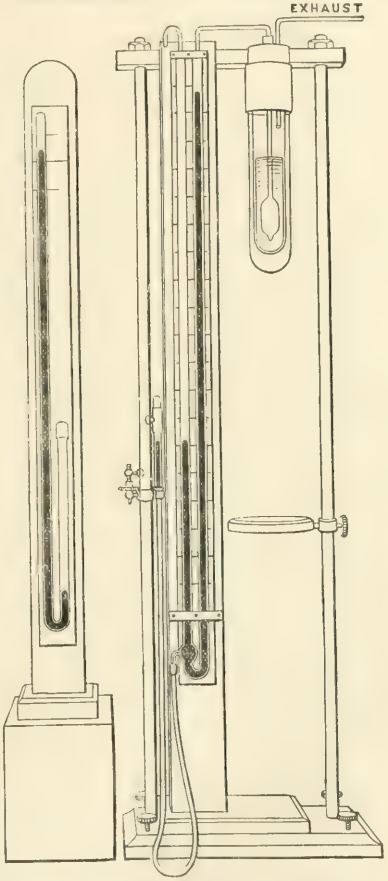
In the present investigation the advantage claimed for the constant pressure gas thermometer over the constant volume thermometer is absent. The effect of high temperature combined with large increase of pressure does not occur in these experiments, where only very low temperatures and a maximum range of pressure of less than one atmosphere were encountered. At the same time, before dispensing with the effect of pressure upon the capacity of the reservoir of the thermometer, it was carefully estimated and found that it could not affect the volume of the reservoir by as much as 1/60,000th part. This being determined a particular advantage results from the use of the constant volume form, because in its case it is unnecessary to know the actual volumes of the reservoir, and of the "outside" space. It is only necessary to know the ratio of these two volumes, and as this ratio appears only in the small terms of the calculation it is not a serious factor in the estimation of such low temperatures.

Two constant volume thermometers (called No. I. and No. II.) were employed, in each of which the volume of the reservoir was about 40 c.c., and the ratio of the outside space to the volume of the reservoir was 1/50 and 1/115 respectively. A figure of the apparatus is given herewith, where A is the thermometric bulb covered with a vacuum vessel to hold the liquid hydrogen, and be exhausted when necessary; B is the manometric arrangement for adjusting the mercury at C to constant volume, and D is the barometer. The readings were made on a fixed scale by means of a telescope with cross-wires and level attached. A similar telescope was permanently fixed on the mark to which the volume had to be adjusted. As the observations had to be made quickly, it was found convenient to use both telescopes on the same massive stand and to read the barometer placed alongside simultaneously.

The formula of reduction used was that given by Chappuis in the "Travaux et Mémoires du Bureau International des Poids et Mesures," tome vi., p. 53, namely,—

$$\left(V_0+\frac{v}{1+at}\right)H_0=\left(\frac{V_0(1+\delta T)+\beta h}{1+at}+\frac{v}{1+at}\right)(H_0+h) \quad . \quad (1),$$

where V_0 is volume of reservoir at 0° C.;
T., temperature of reservoir, measured from 0° C.;
v, volume of "outside" space at the temperature of the room;
t, temperature of the room;
a, coefficient of expansion of the thermometric gas;
β, coefficient of alteration of volume of reservoir, due to change of pressure;
δ, coefficient of expansion of substance of reservoir;
H_0, initial pressure (in these experiments always reduced to 0° C.);
H_0+h, pressure at temperature T., after all corrections have been made.



On putting $\beta=0$ as already explained, equation (1), by algebraic transformation and without any approximation, was altered into the form—

$$T=T_1\frac{273+t+x273}{273+t-x1_1}\,(\text{say})=T_1\theta \quad . \quad . \quad (2),$$

where—

$$T_1=\frac{P-P_0}{aP_0-\delta P} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3),$$

in which P_0 and P replace H_0 and H_0+h, and

$$x=\frac{v}{V_0(1+at)}.$$

* A Paper read before the Royal Society, February 7, 1901.

The gases used as thermometric substances were hydrogen, oxygen, helium, and carbonic acid. The values of α adopted in equation (3) were taken from Chappuis' memoir, and were 0·00366254 for the first three, and 0·00371634 for carbonic acid. The reciprocals of these coefficients are 273·035 and 269·083. The number "273" which appears in θ is so nearly equal to the reciprocal of the former value for α that it was allowed to remain for the first three gases; but in dealing with carbonic acid it was replaced by 269·083.

In these experiments T_I is always negative, and numerically less than 273, so that the value of θ is always greater than unity; nevertheless it differs from it but slightly, its value being unity when $T_I = -273°$ C., and rising to 1·02 when $T_I = 0°$ C. in the case of thermometer No. 1, where $x = 1/50$. It may be noted that when δ is neglected T_I is the usual value given by Boyle's law; there is a convenience therefore in this form of Chappuis' formula for approximation, because T_I can quickly be calculated, and the correcting factor θ can be applied later if desired.

In the first experiment (No. 1 of subjoined Table I.), thermometer No. 1 was filled with electrolytic hydrogen. The initial pressure (the pressure at 0° C.) was almost three-eighths of an atmosphere, and was taken low in order to obviate any complication from condensation on the walls of the reservoir. Two other possible causes might abnormally reduce the pressure at very low temperatures; these were polymerisation, and the presence as impurity of small quantities of gases liquefying above the boiling-point of hydrogen. The measurement of the density of the gas at its boiling-point showed that there was no polymerisation, and further proof of this was evident in the constancy of the value of the boiling-point when different initial pressures were taken. To guard against the presence of gases with a higher boiling-point than hydrogen, the electrolytic hydrogen was allowed to pass continuously for eighteen hours through the thermometric bulb before it was sealed off. It was further calculated that an impurity of oxygen necessary to reduce the boiling-point of hydrogen by a degree would amount to 3 per cent, a quantity too large to escape detection. This experiment gave the boiling-point of oxygen as $-182·2°$, and that of hydrogen as $-253·0°$.

In the second experiment (No. 2) a new thermometer, No. II., was constructed with a much smaller value of x, and as a further protection against the presence of impurities, palladium hydrogen was employed as the source of the gas. A rod of palladium, weighing about 120 grms., kindly placed at my disposal by Mr. George Matthey, F.R.S., was charged with hydrogen in the manner described in my paper "On the Absorption of Hydrogen by Palladium at High Temperatures and Pressures" (*Proc. Chem. Soc.*, 1897), and subsequently used as the source of supply to fill the thermometer. The initial pressure was slightly less than that in the first experiment; the corresponding results were $-182·67°$ and $-253·37°$.*

The new thermometer was filled afresh (No. 4) with palladium hydrogen at an initial pressure rather less than one atmosphere, and gave for the boiling-point of hydrogen the temperature $-252·8°$. This result is a confirmation of the absence of polymerisation.

The next step was to compare these results with the results of similar experiments made upon another gas whose boiling-point fell within the range of easily determined temperatures; and as a further precaution the gas used in the thermometer was the vapour rising from the liquefied gas whose boiling-point was to be determined. The gas first selected was oxygen (No. 5), and as an additional condition to be noted, the initial pressure was made slightly more than an atmosphere, so that it would be in a Van der Waal's "corresponding" state with the hydrogen in the first two experiments, namely, the initial pressure in each case was about 1/50 of the critical pressure. The critical pressure of oxygen was taken about 51 atmospheres, and that of the hydrogen about 18 atmospheres. There are good reasons for believing that the critical pressure of hydrogen is more likely to be about 11 or 12 atmospheres. In the event of the lower value being eventually found the more correct, the effect as between the oxygen thermometer and the hydrogen thermometer will be to make the boiling-point of hydrogen a little too high. The result obtained from this experiment was to place the boiling-point of oxygen at $-182·29°$, thus corroborating in a satisfactory manner the reliability of the method of determining the boiling-point of hydrogen.

The question still remained: How far is a gas thermometer to be trusted at temperatures in the neighbourhood of the boiling-point of the gas with which it is filled? To answer this question the oxygen thermometer was used to determine the boiling-point of liquid air (No. 7) in which a gold-resistance thermometer was simultaneously immersed. The gold thermometer had been previously tested, and found to give correct indications of temperature down to temperatures not only well below the point in question, but lower than those obtainable by any other metal thermometer. In the result the oxygen thermometer gave $-189·62°$, and the gold thermometer $-189·68°$ as the temperature of that particular sample of air boiling at atmospheric pressure.

For another method of comparison this oxygen thermometer was partially discharged (No. 8) until its initial pressure was nearly the same as that in the first hydrogen thermometers. In this state it gave the boiling-point of oxygen as $-182·95°$, establishing again the reliability of the method. All the boiling-points of the liquid gases were made on samples produced at different times.

As an extreme test of the method, I charged the thermometer No. II. with carbonic acid (No. 11) at an initial pressure again a little less than one atmosphere, and used it to determine the boiling-point of dry CO_2; the result was $-78·22°$, which is the correct value.

Hence it appears that either a simple or a compound gas at an initial pressure somewhat less than one atmosphere may be relied on to determine temperatures down to its own boiling-point, in the constant volume gas thermometer.

(To be continued).

* This thermometer gave 99·7° for the boiling-point of water.

TREATMENT OF THE MIXED ORES OF ZINC AND LEAD.

ELLERHAUSEN'S PROCESS.

By E. VILLEJEAN.

Besides the rich ores of lead and zinc, of which the metallurgy is too well known to require mention here, there exist in nature a large quantity of mixed sulphides formed of an intimate mixture of blende and argentiferous galena, which until a few years ago appeared to be unamenable to treatment, as the separation of the lead from the zinc and silver seemed to be impossible without an enormous loss of one or the other of these metals.

The mechanical separation based on the different densities of blende (4) and galena (7·4) is not possible as a matter of fact, except with minerals in a fairly coarse condition; when we have to do with small crystals it only succeeds partially, and with an enormous loss of silver.

The blende retains a large proportion of lead, and its percentage of metallic zinc is hardly more than 35; on the other hand, the galena always retains at least 10 per cent of zinc, which is a great drawback to its ulterior treatment.

The chemical treatment of these mixed ores for the separation of the zinc by an acid after roasting, is too expensive, and has had to be abandoned.

Finally, the separation in the furnace is extremely

difficult; the zinc reduced at the same time as the lead is carried by its volatility to the mouth of the furnace, where it becomes oxidised, forming hard, infusible, and very refractory deposits, which it is absolutely necessary to remove from time to time; this necessitates frequent stoppages and deterioration of the furnace. When the mineral contains more than 12 per cent of zinc it becomes necessary to subject it to a preliminary roasting, or to add to it oxidised minerals, and even in this case it is very inconvenient, as it gives a matt which must be removed, and a pasty slag which causes a considerable loss of lead and silver. In fact, the operation becomes more expensive, and works irregularly.

It therefore became of great importance to try and find a practical and economical method which could be applied to minerals looked upon as poor in zinc and lead, and of which the treatment by ordinary means would not appear to be remunerative. Of such a class are those containing 20 to 30 per cent of zinc, and 15 to 20 per cent of lead, with 0·1 per cent of silver; even to this day such minerals are looked upon as being of no value; producers of lead refuse to treat them because they are not sufficiently rich in metal, and zinc smelters reject them as they contain too much lead.

This difficult problem has now been solved, thanks to the perseverance of M. Ellerhausen, a well known engineer, who has been working on this subject for at least six years. His process has been exhibited in a works at Angoulême, and the results are so satisfactory that it may well be predicted that his method will retain in France an enormous sum of money that is now paid away to other countries, and that the time is not far distant when France will in her turn become an exporter of zinc and lead.

The new process comprises two operations:—1. The simultaneous extraction of the zinc, lead, and silver by volatilisation. 2. The chemical separation of the argentiferous lead in the metallic state, and the zinc in the form of sulphide.

1. *Volatilisation of the Metals.*

The ore is crushed into fragments about the size of an egg, mixed in the usual manner with the necessary amount of coke, carbonate of lime, and oxide of iron, then melted in a blast-furnace. The slag and the matts are run off as in the older methods, but by reason of the high temperature of the furnace the whole of the lead and zinc and a large part of the silver are volatilised; if this latter metal is not entirely removed in the form of vapour it will be found in the matt with the gold and copper which may be present in the ore under treatment.

The difficulty was to remove these metallic fumes and to condense them without loss; Ellerhausen has overcome this difficulty by drawing the fumes off by means of powerful ventilating fans placed in the mouth of the furnace, and into which he injected cold water under very great pressure; this has the effect of condensing them and putting them completely in suspension in the water, which naturally becomes heated, and is then run off into settling vats, when it is cooled previous to being used over again in the ventilating fans, until it is saturated with sulphate of zinc.

We may here remark that the ventilators used were about 1·50 metres in diameter, fitted with copper vanes so that they would remain unattacked, and that they rotated with a speed of 500 revolutions per minute; their capacity must necessarily be greater than that of the blowing-machinery of the blast-furnace, as their function is not only to remove the metallic fumes against a great pressure of water, but also to draw off the products of combustion in the furnace.

The heavy grey deposit formed in the vats consists principally of a mixture of sulphite of lead, sulphide and sulphite of zinc, oxide of zinc, a little carbonate of lime, and oxides of iron, antimony, and arsenic.

The following is the analysis of the deposit from the works at Angoulême:—

Sulphite of lead	67·24
Sulphide of zinc	16·23
Sulphite of zinc	6·63
Oxide of zinc	2·75
Carbonate of lime	2·34
Peroxide of iron	1·00
Oxide of antimony	0·84
Arsenious acid	0·46
Insoluble matter	2·20
Copper	Traces
Silver	220 grms. per ton.

This deposit is collected and dried in the filter-press, but as it still contains about 35 per cent of moisture it is spread out again and slowly dried by means of the waste heat from the blast-furnace.

2. *Separation of the Metals.*

The above-mentioned deposit is gradually added to a solution of raw soda-lye, kept at boiling-point in large iron boilers; a lively effervescence takes place accompanied by a considerable disengagement of heat. When the addition of a further quantity of the deposit provokes no reaction we know that the whole of the lead is reduced to the metallic state, and will be found at the bottom of the boiler together with the silver that was present in the mineral. The zinc, in the form of sulphide, forms a slag with the excess of the free or carbonated soda and the sulphate of soda formed during the operation.

This slag is utilised for the precipitation of the sulphate of zinc, with which the water injected into the ventilators becomes finally saturated, so that eventually we get the whole of the zinc from the original ore in the state of sulphide, hydrate, or carbonate, which can be separated by means of the filter-press from the sulphate of soda which remains in solution. This latter salt is dried and then treated by the Leblanc process for regeneration into raw caustic lye.

As for the mixture of oxide and sulphide of zinc, it is dried separately, roasted, and reduced by the ordinary methods.

Such is, in short, a summary of this remarkable process, of which we will now consider the theory and the advantages.

We will pass rapidly over the reactions which take place in the blast-furnace; they are analogous to those described in the standard books. They may be summed up by saying that the current of warm air at the level of the tuyères, gives rise to the formation of carbonic acid, which is reduced on contact with the red-hot carbon at a higher level, forming carbonic oxide, which sets free metallic iron.

This spongy iron removes a part of the sulphur from the ore, giving sulphide of iron, which we find in the matt combined with sulphide of lead. The ferric oxide which escapes reduction is found in the slag combined with the silica and gangue; it is the same with the lime, of which it is well to have a rather large proportion present so as to keep the lead, zinc, and silver out of the slag.

On the other hand, the atmosphere in the blast-furnace being oxidising, the sulphides are transformed, part into oxides and part into sulphates, which react one on the other, giving the metal and liberating sulphurous gas according to the well-known equations.

Finally, the metals which are volatilised and drawn off by the ventilators, come in contact with oxygen and sulphurous acid in the upper part of the furnace, and are brought into the state of sulphites, as is proved by the analysis we gave above.

It is surprising that even a small portion of the sulphite of lead is not converted into sulphate by the action of the oxygen of the air from the blowing-engine. Neither have we ever found the presence of oxide of lead or of an oxysulphide in the furnace gases; but a portion of the sulphurous gas is transformed into sulphuric acid, in such a manner that the decantation pans end by depositing

sulphate of zinc—about one part of sulphate for three and a half parts of sulphite.

We have seen above that the separation of the lead and zinc rests on the use of a caustic lye—this is perhaps the most interesting point of the whole process; it must be remarked that the caustic lye used is a raw impure one of which the preparation costs very little; it contains hydrate of sodium, as well as carbonate, sulphide, and sulphate of sodium.

In reacting on the deposit, composed principally of sulphites, it reduces the lead and silver to the metallic state, and the metal produced is practically pure, besides being free from antimony and arsenic, which is again a great advantage.

Although the actual equations are, as a general rule, more complicated than those used to show the final reaction, and although in metallurgy especially it is possible to form numerous hypotheses, the author proposes to establish the theory of this operation in the following manner:—

1. The sulphide of sodium transforms the sulphite of lead into sulphide of lead and gives sulphite of sodium; on contact with the caustic soda and the carbonate of soda, the sulphide of lead gives rise to the formation of sulphate of sodium, to a double sulphide of sodium and lead, and to metallic lead, according to the following equations:—

$$7PbS+4Na_2CO_3=Na_2SO_4+3(Na_2S.PbS)+4CO_2+4Pb.$$
$$7PbS+8NaOH=Na_2SO_4=3(Na_2S.PbS)+4H_2O+4Pb.$$

2. At the same time the excess of alkaline hydrate has set free oxide of lead, which reacts on a part of the sulphide of lead, $PbS+2PbO=Pb_3+SO_2$.

3. Another portion of the sulphide of lead reacts on the sulphate of soda, regenerating sulphide of sodium, $2PbS+Na_2SO_4=Na_2S+2SO_2+2Pb$.

It is conceivable that the alkaline sulphide may re-commence a fresh cycle of decomposition in such a manner that the reduction of the lead will continue as long as the strength of the caustic is sufficient, and although the reaction only required a small proportion of sulphide at the commencement.

The process we have just shortly described is in reality but little complicated, and the following advantages must be admitted:—

The whole of the lead and silver is collected, the zinc is separated in the form of a commercial product easy to dispose of; further, the two first of these metals are produced completely free from arsenic and antimony.

The process is applicable to mixed ores which cannot be treated economically by the ordinary methods; it is capable of great extension, subject to having enough land for the construction of sedimentation pans; and, finally, it requires neither fine crushing or preliminary roasting.—*Journ. de Pharm. et de Chim.*, Series 6, vol. xiii., No. 3.

The Colour of Picric Acid and its Solutions.—W. Marckwald.—Picric acid is of a more or less yellow colour, but when crystallised in concentrated hydrochloric acid it is almost colourless; if this latter acid is removed and the picric acid is washed with water it regains its yellow colour. The mother-liquors, which are faintly tinged with yellow, take a much deeper tint on the addition of water. All these phenomena can be explained by the theory of electrolytic dissociation, if we admit that picric acid by itself is quite or nearly colourless, but that the ion $C_6H_2(NO_2)_3O$ is yellow. The different manners in which picric acid behaves can be shown by the following lecture experiment:—When we add yellow commercial picric acid to ligroin we obtain with this non-dissociating solvent a colourless solution which contains very little picric acid. If we remove this liquid and shake it up with several times its volume of water, the latter becomes of an intense yellow colour. Picric acid, when crystallised from a warm saturated solution of ligroin, is almost white.—*Berichte*, vol. xxxiii., p. 1128.

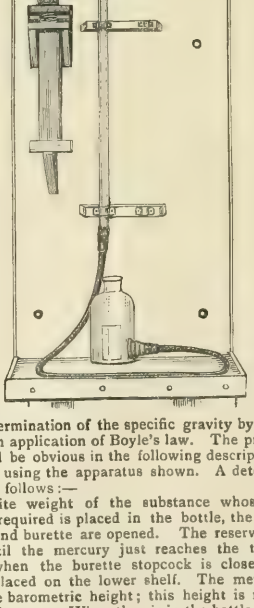
A FORM OF VOLUMOMETER.

By F. W. JONES.

The apparatus shown in the accompanying figure has been found to be a very useful form of volumometer for the determination of the specific gravity of substances which cannot be brought in contact with water. It was designed for the determination of the specific gravity of explosives containing ingredients soluble in water.

The parts are inexpensive and easily procured. They consist of a gas burette with stopcock, connected at one end with a stoppered bottle and at the other end with a reservoir of mercury. The burette shown is a 100 c.c. gas-measuring tube of a Lunge's nitrometer. The bottle is sold as an ozone generator. The bottle must be of small capacity and have two openings in the stopper, one with a stopcock; the stopper must be accurately ground.

The unstoppered opening of the bottle and the burette are connected by stout rubber tubing; the stopper of the bottle being fixed, and the bottle supported by a spring platform. The bottom of the burette is connected with the reservoir of mercury in the usual manner; it is advisable, however, to make the rubber connection with the burette a water joint.



The determination of the specific gravity by a volumometer is an application of Boyle's law. The principle involved will be obvious in the following description of the method of using the apparatus shown. A determination is made as follows:—

A definite weight of the substance whose specific gravity is required is placed in the bottle, the stopcocks of bottle and burette are opened. The reservoir is then raised until the mercury just reaches the top of the burette, when the burette stopcock is closed and the reservoir placed on the lower shelf. The mercury then falls to the barometric height; this height is read off in cubic centimetres. When the air in the bottle has stood long enough to take the temperature of the room, the stopcock of the bottle is closed and that of the burette opened. The mercury immediately falls; the height at which it remains stationary being read off in cubic centimetres; also the rise in the reservoir should be noted.

If V_1 is the gas volume of the bottle and its connections to the burette (P being the barometric pressure), and if v is the volume of gas in the burette at the reduced pressure p, we have the relation according to Boyle's law—

$$V_1 P = (V_1 + v)p;$$

from which—

$$V_1 = \frac{v\,p}{P - p};$$

also—

$$p = d + r;$$

where d = the amount the mercury drops in the burette, and r = the amount the mercury rises in the reservoir. Thus—

$$V_1 = v\,\frac{d + r}{P - d - r}.$$

The burette being of uniform bore, d is ascertained from the observation, when it is known how many cubic centimetres correspond to one inch.

To ascertain the volume occupied by the substance, it is necessary to know the volume of the bottle and its connections to the burette when empty, viz., V; this can be obtained by making a test with the bottle empty. It is advisable, however, to ascertain this figure by making tests with different volumes of mercury. The following figures were obtained with the apparatus shown:—

Bottle containing—	V_1.	V obtained.
	C.c.	C.c.
Empty	109·8	109·8
10 c.c. mercury	100·1	110·1
20 ,, ...	90·2	110·2
30 ,, ...	80·1	110·1
40 ,, ...	70·1	110·1
50 ,, ...	60·2	110·2

If W were the weight of substance taken, then the specific gravity is obviously given by—

$$\text{Specific gravity} = \frac{W}{V - V_1}.$$

The above table shows that, by such an apparatus as figured, specific gravities accurate to the second place of decimals can be obtained.

SOME PRINCIPLES AND METHODS OF ROCK ANALYSIS.*

By W. F. HILLEBRAND.

(Continued from p. 91).

V. *Water—Total or Combined.*

Arguments Against "Loss on Ignition" Method.

In a few cases the simple loss on ignition of a rock will give the total water with accuracy, but in the great majority there are so many possible sources of error that this old-time method can rarely be used with safety. Only when the rock is free from fluorine, chlorine, sulphur, carbon, carbon dioxide, and fixed oxidisable constituents can the loss be accepted as the true index of the amount of water present, and it is rarely that a rock is met with fulfilling these conditions, especially as to the absence of ferrous iron. Blast ignition in presence of carbon dioxide alone of the above list may give a correct result, after separate estimation of the carbon dioxide, provided this emanates from carbonates of the earths and not from those of iron or manganese. The long-maintained and still upheld idea that in presence of ferrous iron a sufficiently correct result is obtainable by adding to the observed loss an amount needed for oxidising all ferrous iron is not justifiable. There can be no certainty that the oxidation has been complete, especially in the case of readily fusible rocks, and at the high temperature of the blast a partial *reduction* of higher oxides is not only possible but sometimes certain. The inability to ensure complete oxidation by simple ignition is illustrated in the case of precipitated ferric hydroxide which has been ignited in contact with its filter-paper. If the quantity was in any degree large it is sometimes decidedly magnetic, presumably from presence of magnetic oxide, which no amount of heating wholly oxidises, especially in the larger grains. Neither is evaporation with nitric acid and re-ignition sufficient to destroy the magnetic property of the oxide, as has been claimed.

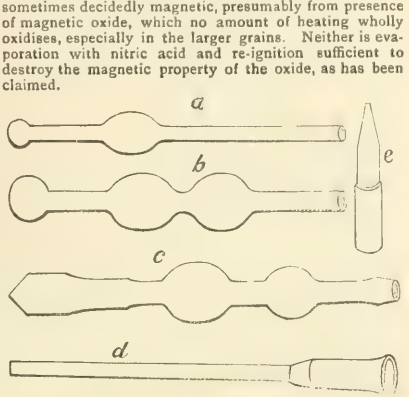


FIG. 4.—PENFIELD'S TUBES FOR WATER DETERMINATION IN MINERALS.

a, *b*, *c*, Different forms of tubes; *d*, thistle tube for introducing the powder; *e*, capillary-tipped stopper.

Direct weighing of the water evolved is then imperative in most cases, and of the numerous methods advocated, or in general use, several will now be considered.

Direct Weighing of the Water Without the use of Absorption Tubes—Penfield's Methods.

For Minerals Easily Deprived of their Water.—If no other volatile constituents than water are present, the beautifully simple method first used by Prof. G. J. Brush, and extended by Prof. S. L. Penfield (*Amer. Journ. Sci.*, 1894, Series 3, vol. xlviii., p. 31; *Zeitsch. für Anorg. Chemie*, 1894, vol. vii., p. 22), leaves nothing to be desired

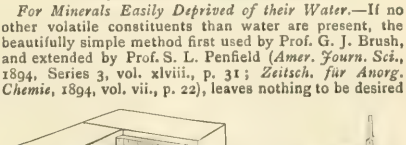


FIG. 5.—PENFIELD'S FIRE-BRICK AND CHARCOAL OVEN FOR USE IN DETERMINING WATER.

for accuracy. It consists simply in heating the powder in a narrow tube of hard glass, enlarged at the closed end, and provided with one or two further enlargements in the middle to hold the water and prevent its running back and cracking the hot glass. A capillary glass stopper fitted in with rubber tubing prevents loss of water by circulating air currents. The tube being held horizontally, the bulb is heated to any required degree by the Bunsen or blast-flame. Moistened filter-paper or cloth wound about the cooler parts of the tube insures condensation of all water. The heated end being finally pulled off, the tube is weighed after cooling and external cleansing, and again after the water has been removed by aspiration. For most rocks,

* *Bulletin of the United States Geological Survey*, No. 176.

as they contain little water, central enlargements of the tube are hardly needed.

Various forms of tubes used by Penfield are shown in Fig. 4.

Before using, even if apparently dry, "these tubes must be thoroughly dried inside, which is best accomplished by heating and aspirating a current of air through them by means of a glass tube reaching to the bottom."

How this simple tube is made to afford entirely satisfactory results with minerals, even when carbonates are present, is fully set forth in the paper cited.

Few rocks, comparatively, are altogether free from other volatile constituents. Hence, for refined work the application of this apparatus in the simple manner above set forth is limited. It may, however, be used with the addition of a retainer for fluorine, sulphur, &c., in the shape of calcium, lead, or bismuth oxides.

For Minerals not Easily Deprived of their Water.—When minerals are present which do not give up their water wholly, even over the blast, as talc, topaz, chondrodite, staurolite, &c., Penfield's simple combination of firebrick and charcoal oven, depicted in Fig. 5, must be used, either with or without a retainer for fluorine, as circumstances demand. The part of the tube in the fire is to be protected by a cylinder of platinum foil tightly sprung about its end, and the part outside by asbestos board, as well as by wet cloth or paper. A piece of charcoal is likewise laid on the tube, as well as beneath and behind, and the blast-flame is given a horizontal direction, so as to play upon the side of the apparatus. In this way a most intense temperature can be reached.

In whichever way the apparatus may be used, the water found is the total water, from which that found separately at 105° C. may be deducted if desired.

(To be continued).

CONCERNING LIPASE, THE FAT-SPLITTING ENZYME, AND THE REVERSIBILITY OF ITS ACTION.*

By J. H. KASTLE and A. S. LOEVENHART.

(Continued from p. 88).

On the Effect of Concentration of the Enzyme on the Velocity of the Reaction.

THE attempt has been made to determine the effect of concentration on the activity of hepatic and pancreatic lipase. According to some observers, the rate of hydrolysis by lipase is proportional to the concentration of the enzyme, especially if the conditions are those most favourable to the reaction. In order to determine the effect of concentration of the enzyme on its activity, concentrated extracts, usually 50 per cent, of the pancreas and liver were prepared, and from these the more dilute extracts, such as 5, 10, 20, and 40 per cent respectively, were made by dilution. Tubes were then prepared containing 4 c.c. of water, 0·1 c.c. of toluene, and 0·19 c.c. of ethylacetate. The tubes were heated for five minutes at 40° C., at the end of which time 1 c.c. of the enzyme of a given concentration was then added, after which the tubes were heated for thirty minutes. They were then removed from the bath and titrated with N/20 KOH. The following results were obtained:—

Concentration of the pancreatic extract. Per cent.	N/20 KOH required. C.c.	Per cent of hydrolysis.
5	0·13	0·33
10	0·25	0·625
20	1·08	2·70
40	2·00	5·00

* From the *American Chemical Journal*, xxiv., No. 6.

Concentration of the hepatic extract. Per cent.	N/20 KOH required. C.c.	Per cent of hydrolysis.
5	0·8	2·00
10	1·35	3·37
20	3·88	9·70
40	6·90	17·25

Still another series, with an extract which was prepared from the pig's liver that had stood for twenty-four hours on ice, gave the following results:—

Conditions of the experiments the same as in the first two series.

Concentration of the hepatic extract. Per cent.	N/20 KOH required. C.c.	Per cent of hydrolysis.
5	1·2	3·00
10	2·02	5·05
20	2·93	7·32
40	4·50	11·25

These results leave no room for doubt that the rate of change increases with the quantity of enzyme present in the solution; in fact, in one of the above series, viz., that of the liver extract, it is approximately proportional to the concentration of the enzyme. The fact, however, must be borne in mind, in the interpretation of the above results, that the fatty acid produced in the hydrolysis of the ethereal salt soon coagulates the proteid present in the solution, and, as has already been pointed out, this coagulation removes the lipase more or less completely from solution; and while the coagulum still possesses considerable lipolytic power, it is doubtful if the enzyme acts to as great advantage as when in solution. We have not yet had the opportunity of comparing the activity of the coagulum with that of the original extract. It is a factor, however, which might very materially vitiate the results, and should certainly be taken into consideration.

On the Effect of the Concentration of the Ethereal Salt on the Velocity of the Reaction.

The hydrolysis of an ethereal salt by lipase certainly presents some analogy at least to the hydrolysis of such a compound by an acid. On account of the instability of the lipase itself, however, its action rather resembles that of the hydrolysis of an ethereal salt by an acid itself so unstable as to be constantly undergoing a gradual decomposition during the change. The question therefore suggests itself in this connection—Is the amount of hydrolysis for any given interval proportional to the active mass of the ethereal salt? Hanriot and Camus (*Comptes Rendus*, 1897, cxxiv., 235) have observed that the rate of hydrolysis varies slightly with the quantity of ethereal salt present. In order to test this point further, the equation for a reaction of the first order,—

$$\frac{1}{\theta} \log \frac{A}{A-x} = k,$$

was applied to the reaction in hand. Tubes containing 4 c.c. of water, 0·1 c.c. toluene, and 0·26 c.c. ethyl butyrate were prepared and heated for five minutes at 40° C. One c.c. of a 10 per cent extract was then added and the tubes heated for the desired length of time and titrated with N/20 KOH. The following results were obtained.

Time. Minutes.	N/20 KOH required. C.c.	Per cent of hydrolysis.	*k.*
5	2·60	6·53	0·01354
10	3·45	8·66	0·00907
15	3·40	8·53	0·00592
20	3·80	9·54	0·00500
25	4·25	10·67	0·00500
30	3·75	9·41	0·00329
60	6·90	17·32	0·00316
120	10·10	25·35	0·00244
180	11·3	28·36	0·00184

One Minute Series.—Conditions the same as in the receding:—

Time. Minutes.	N/20 KOH required.	Per cent of hydrolysis.	k.
1	1·3	3·26	0·03344
2	1·8	4·52	0·02296
3	1·95	4·89	0·01657
4	2·30	5·77	0·01481
5	2·60	6·53	0·01354

The following series was tried to show the effect of varying the amount of ethyl butyrate. The tubes contained 4 c.c. of water, 0·1 c.c. toluene, and 1 c.c. of the 10 per cent liver extract used in the preceding series. The tubes were heated at 40° C. for five minutes, at the end of which time a certain quantity of ethyl butyrate was added and the tubes heated for five minutes at 40° C., and then titrated. The following results were obtained :—

Quantity of ethyl butyrate employed.		N/20 KOH required.	Quantity of ethyl butyrate hydrolysed.
C.c.	Grm.	C.c.	Grm.
0·065 =	0·0575	2·1	0·0122
0·13 =	0·1150	2·7	0·0156
0·195 =	0·1725	2·6	0·0151
0·26 =	0·2300	3·2	0 0185

According to these results, the actual amount of ethyl butyrate hydrolysed by the enzyme in a given time is very largely independent of the concentration of the ethereal salt. It was thought possible that the fact that in all of these experiments a certain amount of the butyrate remained undissolved, might offer an explanation of these results. It was thought desirable, therefore, to repeat some of the work on the concentration of the ethereal salt, using ethyl acetate in the place of ethyl butyrate, for the reason that the former is quite soluble in water. A solution of ethyl acetate was prepared containing 0·01414 grm. of the compound per c.c. 40 c.c. of this solution was placed in a glass-stoppered flask, together with 0·5 c.c. toluene, and heated in the bath at 40° C. until it had reached the temperature of the bath. 10 c.c. of 10 per cent liver extract, which had also been warmed to the temperature of the bath, were then added, and the time of the experiments was reckoned from this instant. The flask was constantly shaken, and at certain intervals 5 c.c. of the mixture were withdrawn from the flask by means of a pipette and titrated with N/20 KOH. The results are given below :—

Time. Minutes.	N/20 KOH required.	Per cent of hydrolysis.	k.
5	0·45	3·50	0·00714
10	0·75	5·83	0·00603
15	0·90	6·99	0·00484
20	1·00	7·77	0·00404
30	1·30	10·10	0·00355
45¼	1·65	12·82	0·00303
60	1·85	14·37	0·00258

The effect of varying the concentration of the ethyl acetate was tried in the following manner :—Ten per cent extract of liver used. Temperature, 40° C. Time, fifteen minutes.

Substance used in experiment.	N/20 KOH required. C.c.	Quantity of ethyl acetate originally present. Grm.	Quantity of ethyl acetate hydrolysed. Grm.
4 c.c. ethyl acetate solution and 1 c.c. of enzyme	0·9	0·05656	0·003952
3 c.c. ethyl acetate solution, 1 c.c. water, and 1 c.c. enzyme..	0·875	0·04242	0·00386:
2 c.c. ethyl acetate solution, 2 c.c. water, and 1 c.c. enzyme..	0·9	0·02828	0·003952
1 c.c. ethyl acetate solution, 3 c.c. water, and 1 c.c. enzyme..	0·775	0·01414	0·003403

It will be observed that, as in the case of ethyl butyrate, the hydrolysis of ethyl acetate by lipase is largely independent of the concentration of the ethereal salt.

In this connection the attempt has also been made to determine whether the hydrolysis of ethyl butyrate by lipase is complete. With this in view, two bottles were prepared as follows :—

No. 1 contained 40 c.c. of water, 10 c.c. of 10 per cent pancreatic extract, 1 c.c. toluene, 0·65 c.c. ethyl butyrate.

No. 2 contained 40 c.c. of water, 10 c.c. of 10 per cent hepatic extract, 1 c.c. toluene, 0·65 c.c. ethyl butyrate.

These were allowed to stand at ordinary temperature for several days. At intervals during this time, 5 c.c. of the contents were withdrawn by means of a pipette and titrated with N/20 KOH. The following results were obtained :—

Time. Hours.	N/20 KOH required. C.c.	Per cent of hydrolysis.
Five c.c. No. 1 (Pancreatic) Lipase.		
19	3·5	35·0
19	3·5	35·0
47	4·3	43·0
47	4·15	41·5
137	4·3	43·0
137	4·3	43·0
Five c.c. No. 2 (Hepatic) Lipase.		
19	7·1	71·0
19	7·25	72·5
47	9·35	93·5
47	9·55	95·5
47	9·4	94·0
137	9·2	92·0

After titration these tubes were allowed to stand for a time. In every case the contents of the tube became acid in reaction, thereby indicating that active enzyme was still present in the solution. The above results are such as to indicate that, except when relatively large amounts of the enzyme are employed, the reaction is incomplete. Whether with lipase of different origin or with varying amounts of the same enzyme the limit reached in all cases would be the same is a matter which can only be settled by further investigation. The fact that the hydrolysis is not complete under ordinary circumstances is in keeping with the more or less regular falling off in the velocity of the reaction described in the above, and is probably to be explained by the fact that the hydrolysis of an ethereal salt by lipase is a reversible process, and that the enzyme, as a catalytic agent, is concerned chiefly in bringing about a condition of chemical equilibrium between the ethereal salt and water and the products of the hydrolysis. Acids also have been found to greatly inhibit the activity of the enzyme, so that the great falling off in the rate of hydrolysis is doubtless, to some extent at least, assignable to this cause.

(To be continued).

A New Hydrate of Alumina.—V. Zunino.—It has already been observed that aluminium when plunged into mercury becomes amalgamated on the surface, and if then left exposed to the air it becomes covered with greyish-white tongue-like protuberances of hydrated alumina containing a little metallic aluminium. The author has analysed this alumina and finds it to be a new hydrate, $Al_2O_3\,5H_2O$. He concludes by remarking that aluminium amalgam, being very easily decomposed by water, might be employed with advantage in organic reductions.—*Gazz. Chim. Ital.*, (1), vol. xxx., p. 194.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 7th, 1901.

Professor Thorpe, C.B., F.R.S., President, in the Chair.

(Concluded from page 94).

*11. "*Organic Derivatives of Phosphoryl Chloride, and the Space Configuration of the Valencies of Phosphorus.*"* By R. M. Caven, B.Sc.

By the interaction of ethoxyphosphoryl chloride, $OP{\cdot}OC_2H_5{:}Cl_2$, with two equivalents of aniline in ethereal solution, a chlorine atom is replaced and *ethoxyanilidophosphoryl chloride*, $OP{\cdot}OC_2H_5{\cdot}NHC_6H_5{\cdot}Cl$, results. This compound crystallises from ether in truncated pyramids, m. p. 61—62°. The remaining chlorine atom may be displaced by the action of *p*-toluidine, when the *ethyl ester* of *anilido*-p-*toluidophosphoric acid*, $OP\,OC_2H_5{\cdot}NHC_6H_5{\cdot}NHC_6H_4CH_3$, is obtained. This substance crystallises from dilute alcohol in needles, m. p. 116°.

p-Toluidine and aniline may be made to react in reverse order. Thus *ethoxy*-p-*toluidophosphoryl chloride* was obtained crystallised in oblique prisms, m. p. 74°; and the *ethyl ester* of p-*toluidoanilidophosphoric acid* was found to crystallise from dilute alcohol in needles, m. p. 116—117°.

The ethyl esters obtained by these reverse processes present similar physical and microscopic characters, and an intimate mixture of the two products melts at 116—117°. Thus the two compounds—

$$OP\begin{cases}OC_2H_5 & (1)\\ NHC_6H_5 & (2)\\ NHC_6H_4CH_3 & (3)\end{cases} \text{ and } OP\begin{cases}OC_2H_5 & (1)\\ NHC_6H_4CH_3 & (2)\\ NHC_6H_5 & (3)\end{cases}$$

are identical, and from this it appears that the two chlorine atoms in the compound $OP{\cdot}OC_2H_5{\cdot}Cl_2$ are similarly situated with regard to the rest of the molecule.

The only alternative to this would be the supposition that, the two chlorine atoms being differently situated, aniline and *p*-toluidine possess the power of appreciating this difference, and exercise a different predilection when reacting with the substance. This supposition, however, can hardly be entertained.

The chlorine atom replaced by the ethoxy-group might, however, differ in relative position from the other two chlorine atoms.

To determine whether this is so, aniline and *p*-toluidine were made to react directly with phosphoryl chloride, and the following compounds were obtained:—*Anilidophosphoryl chloride*, $OP{\cdot}NHC_6H_5{:}Cl_2$, prisms, m. p. 79°; *anilido*-p-*toluidophosphoryl chloride*, $OP{\cdot}NHC_6H_5{\cdot}NHC_6H_4CH_3{\cdot}Cl$, very fine needles, m. p. 133—134°; p-*toluidophosphoryl chloride*, $OP{\cdot}NHC_6H_4CH_3{:}Cl_2$, plates, m. p. 106°; p-*toluidoanilidophosphoryl chloride*, $OP{\cdot}NHC_6H_4CH_3{\cdot}NHC_6H_5{\cdot}Cl$, very fine needles, m. p. 133°. The two substances—

$$OP\begin{cases}NHC_6H_5 & (1)\\ NHC_6H_4CH_3 & (2)\\ Cl & (3)\end{cases} \text{ and } OP\begin{cases}NHC_6H_4CH_3 & (1)\\ NHC_6H_5 & (2)\\ Cl & (3)\end{cases}$$

present similar characteristics, and when mixed together melt at 133—134°. They are therefore identical.

It would seem then that the first and second chlorine atoms to be replaced are similarly situated, and therefore that all three chlorine atoms occupy similar positions within the molecule of phosphoryl chloride. The supposition that the chlorine atom which was at first replaced by the ethoxy-group refuses to react with bases, and is the particular atom which remains intact in these latter compounds, need scarcely be considered.

The above conclusion concerning the similarity of the chlorine atoms, if ultimately established, should be an important factor in settling the configuration of the phosphorus atom.

A tri-derivative, such as—

$$OP\begin{cases}R^{I}\\ R^{II}\\ R^{III}\end{cases},$$

in which the points of attachment of the three radicles are similarly situated in space with reference to the rest of the molecule, does not contain a plane of symmetry. It should therefore be capable of existing in right- and left-handed forms in which the phosphorus atom is the centre of optical activity. Experiments are now in progress to determine this point, and the fact that one of the elements is doubly bound to the phosphorus atom lends additional interest to the investigation, which was commenced at the suggestion of Dr. Kipping.

*12. *α-Hydroxycamphorcarboxylic Acid.*"* By A. Lapworth and E. M. Chapman.

An account was given of experiments begun with the view of preparing α-bromohomocamphoric acid, an object which has been achieved in another way (*Trans.*, 1900, lxxvii., 1063).

A method for preparing camphorquinone in large quantities, and free from camphoric anhydride, was described. *Camphorquinone*-p-*bromophenylhydrazone*, $C_{10}H_{14}O{:}N_2H{\cdot}C_6H_4Br$, is eminently suited for the detection of the quinone in small quantities; it is very sparingly soluble in nearly all organic media, and melts at 215—216°. It appears to exist only as the ketonic modification (Betti, *Ber.*, 1899, xxxii., 1995). *Camphorquinonesemicarbazone*, $C_{10}H_{14}O{:}N_2H{\cdot}CONH_2$, which is nearly colourless at ordinary temperatures, turns yellow at 210°, melts and decomposes at 228—229°.

When camphorquinone is treated with hydrogen cyanide at −10°, a nearly colourless mass is produced, which probably consists of stereoisomeric forms of *α-dihydroxycyanocamphor*,—

$$C_8H_{14}\begin{cases}C(OH)CN\\ CO\end{cases}.$$

One of these was isolated in the form of six-sided plates, which decomposed when heated, and melted at 197—198°, approximately the melting-point of camphorquinone; it had all the properties of an α-hydroxynitrile, and when dissolved in fuming sulphuric acid was converted into *α-hydroxycamphorcarboxylic amide*,—

$$C_8H_{14}\begin{cases}C(OH)CONH_2\\ CO\end{cases},$$

which forms large brilliant crystals, melting somewhat indefinitely, at 235—240°.

α-Hydroxycamphorcarboxylic acid,—

$$C_8H_{14}\begin{cases}C(OH)CO_2H\\ CO\end{cases},$$

is formed on heating the nitrile with strong hydrobromic acid for some time. It is sparingly soluble in water, and crystallises in brilliant needles or prisms which melt and decompose at 207—208°, becoming converted into Manasse's hydrocamphor (*Ber.*, 1897, xxx., 659). The acid is converted into carbon dioxide and camphorquinone by lead peroxide and acetic acid, and is slowly decomposed when heated with alkalis, being, perhaps, converted into *di*α-homocamphanic acid (*Trans.*, 1900, lxxvii., 1067).

α-Acetoxycamphorcarboxylic acid,—

$$C_8H_{14}\begin{cases}C(OAc)CO_2H\\ CO\end{cases},$$

melts at 85—86°.

It was pointed out that these compounds must contain the carboxyl group in the position in which it occurs in camphor.

*13. "*The Bacterial Decomposition of Formic Acid.*"* By W. C. C. Pakes and W. H. Jollyman.

The authors, as the result of various observations, were

led to analyse the gases produced from sodium formate in solution by certain bacteria. These experiments show that hydrogen and carbon dioxide are evolved, sodium hydrogen carbonate remaining in the medium in which the sodium formate was dissolved. The total amount of carbon dioxide, that is, the amount evolved as a gas and that in combination, was found to be equal in volume to the amount of hydrogen evolved. It is therefore possible to express the reaction by a very simple equation, either $H\cdot CO_2Na + H_2O = NaHCO_3 + H_2$ or $H\cdot CO_2H = CO_2 + H_2$. One of the chief reasons why the addition of sodium formate to media containing dextrose is of such advantage is that the alkali formed from the decomposition of the sodium formate neutralises the acids produced by the decomposition of the sugar; the fact that the medium continues to be neutral or alkaline allows the bacteria to grow for a longer period than when the medium becomes increasingly acid.

Many bacteria had no action upon the formate, and it was found that none of the more commonly occurring yeasts had any action upon the salt.

14 "*Preparation of Substituted Amides from the Corresponding Sodamide.*" By A. W. Titherley, M.Sc., Ph.D.

The behaviour of sodamide derivatives of the type $R\cdot CO\cdot NHNa$ with various halogen organic compounds was investigated, when the marked difference observed between the aliphatic and aromatic derivatives suggested a dissimilarity in their constitution.

(*a*) With alkyl haloids. In presence of benzene there is no action; alcohol, if present, takes part in the reaction, giving the amide and an ether, thus:—

$$CH_3\cdot CO\cdot NHNa + C_2H_5OH + C_2H_5I = CH_3CO\cdot NH_2 + NaI + C_2H_5OC_2H_5.$$

Sodiobenzamide in sealed tubes at 140° readily gives alkyl derivatives, $C_6H_5CO\cdot NHR$, in absence of alcohol, whilst sodacetamide under similar conditions undergoes complex decomposition, giving only a small quantity of the alkylacetamide.

(*b*) With acid chlorides in presence of benzene, sodiobenzamide behaves normally, giving diamides, $C_6H_5CO\cdot NH\cdot COR$, but sodacetamide does not give regular results. With acetyl chloride, diacetamide is formed, but with benzoyl chloride a complex change takes place, dibenzamide, tribenzamide, acetamide, diacetamide, benzonitrile, and benzoic anhydride being formed, but no acetyl benzamide.

(*c*) With halogen esters, sodiobenzamide behaves normally, but gives only small yields of direct condensation products. Ethyl hippurate was synthesised by the action of ethyl bromacetate on sodiobenzamide. Sodacetamide gives unsatisfactory results.

(*d*) With bromamides, symmetrical disubstituted acyl hydrazines were expected, in accordance with the equation $R\cdot CO\cdot NHNa + R\cdot CO\cdot NHBr = R\cdot CO\cdot NH\cdot NH\,CO\cdot R + NaBr$; but no trace of these substances was obtained, as both aliphatic and aromatic derivatives immediately undergo molecular re-arrangement, giving alkyl acyl ureas, $NHR\cdot CO\cdot NH\cdot COR$.

It was found that the sodium atom could be best replaced by alkyl radicles by heating with potassium alkyl sulphates; for example:—

With sodamide, amines are formed thus:—

$$NaNH_2 + KRSO_4 = R\cdot NH_2 + KNaSO_4.$$

With sodium organic amides, substituted amides are formed:—

$$CH_3\cdot CO\cdot NHNa + KRSO_4 = CH_3\cdot CO\cdot NHR + KNaSO_4.$$

On treatment with sodamide, the remaining hydrogen atom in the group CONHR may be replaced by sodium, and this similarly replaced by an alkyl group. The stages are:—

$$R\cdot CO\cdot NH_2 \rightarrow R\cdot CO\cdot NHNa — R\cdot CO\cdot NHR^{I} \rightarrow R\,CO\cdot NNaR^{I} \rightarrow R\cdot CO\cdot NR^{I}R^{II},$$

where R^{I} and R^{II} may be similar or dissimilar radicles.

Several new monalkyl amides and mixed dialkyl amides have been thus prepared, and their behaviour, with dry hydrochloric acid and sodamide respectively, studied. The hydrochlorides of the monalkyl amides contain base and acid in the proportion of 1 mol.: 1 mol. (compare acetamide hydrochloride), and in the aliphatic group are solid, crystalline, very easily fusible, fairly stable substances; in the aromatic group, thick viscid liquids, which dissociate readily.

Acetethylamide hydrochloride, $CH_3\cdot CO\cdot NHC_2H_5,HCl$, melts at 60°; and *acet-n-propylamide hydrochloride*, $CH_3\cdot CO\cdot NHC_3H_7,HCl$, melts at 47°; *acetisobutylamide*, $CH_3\cdot CONH\cdot C_4H_9\beta$, is a liquid boiling at 225—227°, is miscible with water, but is readily separated as an oil by adding alkali; its hydrochloride melts at 107°.

Benz-n-propylamide, $C_6H_5\cdot CO\cdot NHC_3H_7$, crystallises in cubic-shaped crystals melting at 84·5°, and boiling at 294—295°.

Benzbutylamide, $C_6H_5\cdot CO\cdot NHC_4H_9$, melts at 57°, and boils with slight decomposition at 295—296°. *Acetmethylethylamide*, $CH_3\cdot CO\cdot N(CH_3)C_2H_5$, boils at 180°; and *benzmethylethylamide*, $C_6H_5\cdot CO\cdot N(CH_3)C_2H_5$, boils at 280°. Both are liquids. The sodium derivatives, $R\cdot CO\cdot NNaR^{I}$, are white powders, appreciably soluble in benzene. In the aliphatic series they dissolve unchanged in alcohol, and the solutions give, with alcoholic silver nitrate, *orange* precipitates. The aromatic sodium alkyl amides are decomposed by alcohol.

The author discussed the tautomerism of the amides and expressed the view that in the aliphatic group the sodium compounds are true sodamide derivatives of the type $R\cdot CO\cdot NHNa$, whilst in the aromatic group they are partly sodium salts of the imidehydroxy-formula,—

$$R\cdot C\overset{NH}{\underset{ONa}{\leqslant}},$$

and partly $R\cdot CO\cdot NHNa$. Two series of silver derivatives have been obtained, one white, presumably—

$$R\cdot C\overset{NH}{\underset{OAg}{\leqslant}},$$

and the other orange,—

$$R\cdot C\overset{O}{\underset{NHAg}{\leqslant}},$$

which are capable of passing into each other and are very unstable.

The formula of benzamide itself in aqueous solution is probably—

$$C_6H_5\cdot C\overset{NH}{\underset{OH}{\leqslant}},$$

and that of acetamide, $CH_3\cdot CO\cdot NH_2$.

15. "*Note on Two Molecular Compounds of Acetamide.*" By A. W. Titherley, M.Sc., Ph.D.

Acetamide sodium bromide, $2CH_3\cdot CONH_2,NaBr$, and acetamide sodium iodide, $2CH_3\cdot CONH_2,NaI$, are well defined crystalline compounds analogous to the hydrochloride, $2CH_3\cdot CONH_2,HCl$. They were obtained as by-products in certain reactions, and may be prepared by direct union of the constituents in the presence of alcohol. On concentration or cooling they separate as needles which begin to dissociate below their melting points and are very deliquescent. On quickly heating, $2CH_3\cdot CONH_2,NaBr$ melts at 144° with separation of NaBr, and $2CH_3\cdot CONH_2,NaI$ melts at 110° with separation of NaI. Molecular compounds with other haloid compounds of potassium and sodium do not appear to exist.

16. "*Diacetamide; a New Method of Preparation.*" By A. W. Titherley, M.Sc., Ph.D.

Diacetamide may be readily prepared by the direct action of acetyl chloride (in benzene solution) on acetamide,—

$$3CH_3CONH_2 + CH_3COCl = (CH_3CO)_2NH + 2(CH_3\cdot CONH_2)HCl.$$

After filtering off the insoluble acetamide hydrochloride and removing the benzene by distillation the residue is

fractionated. No previous account appears to have been given of this reaction.

Neither acetyl nor benzoyl chloride has any action on benzamide, but the benzoyl chloride gradually decomposes acetamide, with formation of benzoic acid, benzoic anhydride, and acetonitrile.

17. "*Organic Derivatives of Silicon.*" By F. S. Kipping and L. L. Lloyd.

Experiments on the preparation of enantiomorphously related silicon compounds were commenced nearly three years ago, and a short account of this work has already appeared (*Proc.*, 1899, xv., 174); the much more important object, the separation of the isomerides, has not yet been attained.

When silicon tetrachloride is treated in dilute ethereal solution with one molecular proportion of a phenol or alcohol, it is decomposed in accordance with the equation $SiCl_4 + R^I \cdot OH = SiCl_3 \cdot OR^I + HCl$, and by submitting the product to a similar treatment, a second group, and then a third, may be introduced,—

$SiCl_3 \cdot OR^I + R^{II} \cdot OH = SiCl_2(OR^I)(OR^{II}) + HCl.$

$SiCl_2(OR^I)(OR^{II}) + R^{III} \cdot OH = SiCl(OR^I)(OR^{II})(OR^{III}) + HCl.$

Amido-compounds may be used in the above reactions in the place of alcohols or phenols with similar results.

Phenoxymethoxysilicon dichloride, $SiCl_2(OPh)(OMe)$ (b. p. 216°), and *phenoxymethoxyethoxysilicon chloride*, $SiCl(OPh)(OMe)(OEt)$ (b. p. 241°), are colourless, oily liquids readily decomposed by water; *methoxyethoxysilicon dichloride*, $SiCl_2(OMe)(OEt)$, and *methoxyethoxyisobutoxysilicon chloride*, $SiCl(OMe)(OEt)(OBu\beta)$, boiling at 128° and 160° respectively, have similar properties.

The principle on which the above reactions are based, namely, the interaction of halogen compounds and hydroxylic or amido-derivatives, is evidently capable of general application, and its use for the preparation of enantiomorphously related compounds is being investigated by one of us in the case of elements other than silicon.

18. "*Isomeric Hydrindamine Camphor-π-Sulphonates. Racemisation of α-Bromocamphor.*" By F. S. Kipping.

In examining the salt formed by the combination of *d-l*-hydrindamine with *d*-camphor-π-sulphonic acid (obtained by the reduction of *α*-bromocamphorsulphonic acid) in order to try and isolate isomeric salts analogous to those obtained from the bromo-acid (*Trans.*, 1900, lxxvii., 861), it was found that although the salt at first seemed to be homogeneous, it could be resolved into fractions having different specific rotations.

This difference in optical properties is due to the fact that the crude *d* camphor-π-sulphonic acid contains a very small quantity of the enantiomorphously related isomeride, and as the latter can hardly have been produced during the reduction of the bromocamphorsulphonic acid, it follows that *α*-bromocamphor undergoes partial racemisation during sulphonation.

This change is one of considerable complexity, and necessitates the transference of part of one of the closed chains in bromocamphor from one position to another, as in the case of the optical inversion of camphor (Kipping and Pope, *Trans.*, 1897, lxxi., 958).

Except for the separation already referred to, the salt of *d-l*-hydrindamine with camphor-π-sulphonic acid undergoes no change on fractional crystallisation, and gives a molecular rotation practically identical with that of ammonium *d*-camphor-π-sulphonate; it is therefore a *partially* externally compensated salt of the type *d*AlB,*d*AdB; it crystallises from water in large transparent rhomboidal prisms containing water of crystallisation, and melts at about 198°.

19. "*Tetramethylene Carbinol.*" By W. H. Perkin, jun.

When the chloride of tetramethylenecarboxylic acid is reduced in moist ethereal solution with sodium, it is converted into tetramethylene carbinol,—

$$\begin{array}{l} CH_2 \cdot CH_2 \\ | \quad | \\ CH_2 \cdot CH \cdot CH_2OH \end{array}$$

a colourless oil boiling at 143—144°, and having an odour resembling that of isoamyl alcohol. The determinations of the density, refraction, and magnetic rotation of this substance are given in the detailed paper.

PHYSICAL SOCIETY.

Ordinary Meeting, February 22nd, 1901.

Prof. S. P. Thompson, President, in the Chair.

A paper on "*How Air Subjected to X-Rays Loses its Discharging Property, and how it Discharges Electricity*," by Prof. Emilio Villari (Hon. Fellow), was read by the Chairman.

Air made active by X-rays in passing through a long tube coiled in many turns loses much more of its discharging power than it does in passing through the same tube if straight. During this process the tube charges itself to a certain potential. If active air is allowed to stream on masses of wire gauze or wound-up ribbons, enclosed in tubes, the metals, independent of their nature, take a positive or negative charge according to whether the active air rubs against them with force or lightly. Experiments have been performed to prove this. For instance, tubes of copper or lead, if short and straight, take negative charges, but if long and coiled they take positive charges. These phenomena cannot be attributed to chemical actions, but seem to be produced by a special rubbing of the active air upon metallic surfaces, as the result of which they assume one of the charges, and the other charge ought to manifest itself in the air. This is not the case, the charge of the air being often of the same kind as that of the metals. It has previously been shown by the author that active air by streaming against an electrified body is reduced either to ordinary air or to air charged with the electricity which disappears. Hence it may be supposed that the active air in rubbing upon the metallic surfaces develops the two electricities, one of which manifests itself upon these surfaces, and the other goes to reduce the active air to ordinary air, and therefore does not become manifest. The electroscope used in the experiments consisted of a fixed brass-plate, and a gold leaf, whose position was determined by means of a telescope with an eye-piece scale.

The Chairman said he had observed the fact that metals were charged sometimes positively and sometimes negatively by active air.

Mr. Watson asked if any experiments had been performed on the viscosity of gases rendered active by X-rays.

A paper on "*The Propagation of Cusped Waves and their Relation to the Primary and Secondary Focal Lines*," by Prof. R. W. Wood, was read by Mr. Watson.

This paper is a discussion of the reflexion of a plane-wave by a hemispherical mirror, the reflected wave being likened to a volcanic cone. The cusp of the wave, or the rim of the crater, traces the caustic, and is continuously passing through a focus. This accounts for the increased illumination along the caustic. The wave-fronts were drawn by constructing the orthogonal surface, which in section is an epicycloid. The evolute of this curve is the caustic, and the reflected wave-fronts form a family of parallel curves which are the involutes of the caustic. The wave-front between two focal lines is expanding along one meridian, and contracting along a meridian at right angles to it; in other words, the wave is convex along one meridian and concave along the other. The outer slope of the volcanic cone representing the reflected wave corresponds to the position of the wave-front between the focal lines. A useful piece of apparatus can be made by silvering the outside of a hemispherical glass vessel,

The concave mirror thus formed should be mounted on a stand and a small electric lamp arranged so that it can move along the axis of the mirror. A spherical wave starting at the focus of a hemispherical mirror is reflected as a saucer-shaped wave, the curved sides of the saucer coming to a focus in a ring surrounding the nearly flat circular bottom. If the lamp is placed at the focus the luminous ring and the uniformly illuminated area within it can be shown on a ground glass screen. If the lamp be moved to a point midway between the focus and the the mirror a ring of intense brilliance, with very little light within it, is formed.

A paper on "*Cyanine Prisms*," by Prof. R. W. Wood, was read by Mr. Watson.

Prof. Wood has already described a method of making prisms of solid cyanine by pressing the fused dye between plates of glass. Until recently angles of about half a degree were the largest that could be used with advantage on account of the small quantity of green light transmitted. A new supply of the dye has been found to transmit a large quantity of green light with an angle of over one degree. By viewing the filament of an incandescent electric lamp through one of these prisms the anomalous spectrum is seen, the colours being arranged in the order:—Green, blue, violet, red, orange. Prof. Wood has crossed one of these prisms with a photographic copy of a diffraction grating having 2000 lines to the inch. On viewing a naked arc lamp the diffraction spectra are deviated by the prism, the red ends being turned up, and the blue-green ends turned down.

The Chairman said he had been trying to obtain some cyanine, but had not succeeded. Rosaniline has an anomalous dispersion, but cannot be fused. The acetate of rosaniline might, however, be used.

The Society then adjourned until March 8th.

CORRESPONDENCE.

ARSENIC IN SULPHURIC ACID.

To the Editor of the Chemical News.

Sir,—With reference to the evidence of Dr. Campbell Brown before the Liverpool Coroner at a recent inquest on a death from arsenical poisoning:—

The percentage of arsenic (As_2O_3) found in the samples supplied to Messrs. Bostock was excessively high; the following are the figures:—

1·92, 2·36, 2·24, and 2·5 per cent.

In all my experience as a chemist and practical vitriol maker, I have never come across such high percentages as these.

The most impure acid in any factory is that concentrated in the "Glover tower," where it meets all the dust and gases from the kilns; this acid seldom contains more than from 0·5 to 1 per cent of arsenic (As_2O_3). Acid from the chambers contains from 0·02 to 0·1 per cent.

It would be instructive to know how the vitriol in question was manufactured, and from what kind of pyrites.

It was interesting to note that Dr. Campbell Brown found the arsenic depositing in crystals on the sides of the carboys.

White arsenic (As_2O_3) is only sparingly soluble in cold strong vitriol, but much more readily so in hot, from which it deposits in crystals on the sides and bottom of the vessel on cooling.

I have never noticed any crystals deposited on the sides of the carboys used for ordinary strong "commercial" acid.—I am, &c.,

Geo. H. Allibon, F.C.S.

Belfast, February 18, 1901.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxii., No. 5, February 4, 1901.

Origin of Chemical Combination. Allotropic Forms of Silver.—M. Berthelot.—The author's method of examining the different allotropic forms of silver consists in measuring the heat brought into action when the metal in its different states is dissolved in an equal weight of mercury. Mercury is employed as a liquid calorimeter, and used at ordinary temperatures. The differences between the quantities of heat thus observed are equal to the heats of transformation of one state into another. The various allotropic forms of silver on which the above experiments were made were:—(1) Beaten silver in thin sheets; (2) silver produced by the transformation of the beaten silver when kept in a current of oxygen for about twenty hours at 500° to 550°; (3) crystalline silver in the form of needles (prepared by the slow electrolysis of silver nitrate dissolved in 10 parts of water); (4) silver precipitated by a sheet of copper by means of silver nitrate in dilute solution. This precipitate is then washed and dried—one portion at the ordinary temperature, the other at 120°; (5) the silver prepared as in No. 4, but heated to a dull red heat.

Researches on the Compounds of Silver and Mercury.—M. Berthelot.—The research described in the former paper suggested to the author the idea of examining the heat of formation of the various amalgams of silver; some being crystalline, and obtained when silver is precipitated from its nitrate by means of mercury, the others prepared by pounding the two metals together in a mortar. In all cases it is found that the chemical affinity of silver for mercury is very slight. A series of crystalline amalgams can be formed simply by varying the relative proportions of the two metals—for 1 atom of mercury, from 1 atom of silver up to 50 atoms. The crystals of these amalgams seem to form in this case in the same manner as in other cases of mixtures of isomorphous salts, which crystallise together in all proportions.

Borates of Magnesium and the Metals of the Alkaline Earths.—L. Ouvrard.—In a former paper, the author describes his researches on the preparation of the tribasic borates of a certain number of metals. Since then he has applied the same method to magnesium and the metals of the alkaline earths—metals which appear to less easily lend themselves to the preparation of crystalline products. Magnesium dissolves easily in melted boric anhydride. Lime or its carbonate dissolves equally well at a red heat in a mixture of boric anhydride and fluorhydrate of potassium fluoride, but the well-defined product is only obtained by using three molecules of lime to one of each of the other compounds. Strontia and baryta behave in an almost similar manner with regard to the above mixture. By their addition in suitable proportions, $B_2O_3.3SrO$ and $B_2O_3.3BaO$ separate out on cooling in the form of crystals which act on polarised light and are less acted upon by water than the corresponding calcium salt, very slightly attacked by dilute acetic acid, but very soluble in mineral acids.

Electrolysis of Oxy-acids. Preparation of β-Amyloxypropionic Acid and the Diamyline of Butanediol-1.4.—J. Hamonet.—The author applies to the preparation of some glycols or their ethers the decomposition of the alkaline salts of the oxy-acids by means of the electric current. If the ether-oxide group of the molecule is in the β-position, the reaction takes place almost according to the equation $2ROC_nH_mCO_2K = K_2 + 2CO_2 + (ROC_nH_m - C_nH_mOR)$; but if this group is in the α-position, a great portion of the ether is hydrolysed,—

$RCH(OC_5H_{11})CO_2H + H_2O = (RCHOHCO_2H) + C_5H_{11}OH.$

In the present paper, only the reactions which take place according to the first equation are considered. By a modification of the above method, β-amyloxypropionic acid, $C_5H_{11}OCH_2CH_2CO_2H$, was prepared, and from this, again, amyl-β-chloropropionate was prepared—a substance which is easily transformed into amyl-β-amyloxypropionate by the addition of sodium amylate dissolved in amyl alcohol.

MISCELLANEOUS.

Arsenic in Beer.—We have received the report of the Public Analyst to the City of Manchester for the quarter ending December 31st, 1900. Among other articles examined we note that 52 samples of beer were tested for arsenious acid; of these, 13 were genuine, while the others contained arsenious acid in quantities varying from one-seventh of a grain per gallon to traces only.

The Sulphocyanacetic Acids.—G. Frerichs and H. Beckurts.—When we react with NCSK on chloracetylurethane we obtain two isomers—

$CH_2.CONH.COOR$ and $CH_2CONH.COOR$
| |
$N=C=S$ $S-C\equiv N$

Isosulphocyanacetylurethane. Sulphocyanacetylurethane.

The salts obtained by Claesson by reacting with NCSK on CH_2ClCO_2M, as well as the ethers derived from them, correspond not only with the normal sulphocyanacetic acid, but also with its isomer, isosulphocyanacetic acid. The amides, on the contrary, correspond only with the normal acid. The salts, as well as the ethers, give with warm alkaline lyes yellowish-red solutions, which give off HCN and H_2S when acidulated, and do not form thioglycolic acid, CH_2SH-CH_2COOH; these are the characteristics of the iso-derivatives. The corresponding acetic amide, treated in the same manner, does not give off HCN, but forms thiogycolic acid; it has the character of a derivative of the normal acid, S being attached directly to the radical which prevents its disengagement in the form of SH_2.—*Arch. d. Pharm.*, vol. ccxxxviii., pp. 9—15.

MEETINGS FOR THE WEEK.

MONDAY, 4th.—Society of Arts, 8. (Cantor Lectures). "The Bearings of Geometry on the Chemistry of Fermentation," by W. J. Pope.
—— Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. Adjourned Discussion on the "Occurrence and the Detection of Arsenic in Manufactured Products." "A New System for the Manufacture of Borax and Nitrates," by Dr. W. Newton, F.I.C. (time permitting).

TUESDAY, 5th.—Royal Institution, 3. "The Cell as the Unit of Life," by Allan Macfadyen, M.D., B.Sc.
—— Society of Arts, 8. "Early Playing Cards and their Decoration," by Richard Steele.

WEDNESDAY, 6th.—Society of Arts, 8. "Modern Artillery," by Lieut. Arthur Trevor Dawson, late R.N.
—— Society of Public Analysts, 8. "The Determination of Dissolved Oxygen in Water in presence of Nitrites and Organic Matter," by S. Rideal, D.Sc., F.I.C. "Some Analyses of Oatmeal," by Bernard Dyer, D.Sc., F.I.C. "The Detection and Estimation of Preservatives in Milk," by M. Wyner Blyth, B.A., B.Sc.

THURSDAY, 7th.—Chemical, 8. "Nomenclature of the Acid Esters of Unsymmetrical Dibasic Acids," "Additive Compounds of α- and β-Naphthylamine with Trinitrobenzene Derivatives," and "Acetylation of Arylamines," by J. J. Sudborough. "Formation of Amides from Aldehydes," by R. H. Pickard and W. Carter.
—— Royal Institution, 3. "Greek and Roman Portrait Sculpture," by Prof. Percy Gardner, Litt.D.

FRIDAY, 8th.—Royal Institution, 9. "Vitrified Quartz," by W. A. Shenstone, F.R.S.
—— Physical, 5. "A Theory of Colloidal Solutions," by Dr. F. G. Donnan. Exhibition of Apparatus, by R. Appleyard. "Production of a Bright Line Spectrum by Anomalous Dispersion and its application to the 'Flash Spectrum,'" by Prof. R. W. Wood.

SATURDAY, 9th.—Royal Institution, 3. "Sound and Vibrations," by the Rt. Hon. Lord Rayleigh, F.R.S., &c.

THE
DAVY FARADAY RESEARCH LABORATORY
OF
THE ROYAL INSTITUTION.

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The Right Hon. LORD RAYLEIGH, M.A., D.C.L., LL.D., F.R.S.
Professor DEWAR, M.A., LL.D., F.R.S.

Superintendent of the Laboratory:
Dr. ALEXANDER SCOTT, M.A., D.Sc., F.R.S.

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THE CHEMICAL NEWS.

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THE BOILING-POINT OF LIQUID HYDROGEN, DETERMINED BY HYDROGEN AND HELIUM GAS THERMOMETERS.*

By JAMES DEWAR, M.A., LL.D.,
Professor of Chemistry at the Royal Institution, and Jacksonian Professor, University of Cambridge.

(Concluded from page 98).

ANOTHER thermometric substance at our disposal, as suitable for determining the boiling-point of hydrogen as hydrogen had been in determining that of oxygen and other gases, is helium. The early experiments of Olszewski and my own later ones showed that pure helium is less condensible than hydrogen, and that the production of liquid or solid products by cooling Bath helium to the temperatures of boiling and solid hydrogen was only partial, and resulted from the presence of other gases undefined at the time the experiments were made. The mode of separating the helium from the gases given given off by the King's Well at Bath is fully described in my paper on "The Liquefaction of Air and the Detection of Impurities" (*Proc. Chem. Soc.*, 1897; CHEMICAL NEWS, lxxvi., 272).

If the neon, present as impurity in the Bath helium which was used, should reach its saturation pressure about the boiling-point of hydrogen, the values given by this thermometer of the boiling-point of hydrogen would be too low. In order to avoid this, the crude helium extracted from the Bath gas was passed through a U-tube cooled by liquid hydrogen to condense out the known impurities—oxygen, nitrogen, and argon. In my paper "On the Application of Liquid Hydrogen to the Production of High Vacua" (*Roy. Soc. Proc.*, 1898; CHEMICAL NEWS, lxxix., 73), it was shown that at the temperature of boiling hydrogen, oxygen, nitrogen, and argon have no measurable tension of vapour, and that the only known gases uncondensed in air after such cooling were hydrogen, helium, and neon. This same neon material occurs in the gas derived from the Bath wells. A sample of helium prepared as above described, which had been passed over red-hot oxide of copper to remove any hydrogen, was found by Lord Rayleigh to have a refractivity of 0·132. The refractivity of Ramsay's pure helium being 0·1238, and that of neon 0·2345, it results that my helium contained some 7·4 per cent of neon, according to the refractivity measurements. This would make the partial tension of the neon in the helium thermometer cooled in the liquid hydrogen to be about 4 m.m., and this being taken as the saturation pressure the boiling-point of neon is about 34° absolute. The initial pressure (No. 9) was taken rather less than an atmosphere, and the temperature of the boiling-point of hydrogen was given by this thermometer as −252·68°. A further observation (No. 10) was taken on another occasion with the same thermometer, and the value found was −252·84°. The fact that the boiling-point of hydrogen, as determined by the helium thermometer, is in substantial agreement with the results obtained by the use of hydrogen itself is a conclusive proof that no partial condensation of the neon had occurred.

Of the remaining experiments in Table I., No. 3 was made in order to show the effect of a very small initial pressure, one-sixth of an atmosphere. The results were unsatisfactory, owing to the sticking of the long columns of mercury giving uncertain pressure readings. In this

TABLE I.

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10	11.
Thermometer $x = -\frac{\alpha_0}{V_0}$	No. I.	No. II.	No. II.	No. II.	No. I.	No. I.	No. I.	No. I.	No. II.	No. II.	No. II.
	x^0_0	x^{12}_0	x^{12}_0	x^{12}_0	x^0_0	x^0_0	x^0_0	x^0_0	x^{12}_0	x^{12}_0	x^{12}_0
Substance.	Electrolytic hydrogen.	Palladium hydrogen.	Palladium hydrogen.	Palladium hydrogen.	Oxygen.	Oxygen.	Oxygen.	Oxygen.	Helium (Bath).	Helium (Bath).	Carbonic acid.
Barometer	760·6	764·4	759·5	770·5	772·5	756·0	766·0	753·5	765·0	770·0	759·0
Temperature of room	13°	13°	21°	12°	13·6°	12°	13·3°	15°	15°	13°	
Pressures at 0° C.	M.m.	M.m.	M.m.	M.m.	M.m.	M.m.	M.m.	M.m.	M.m.	M.m.	M.m.
B.P. of carbonic acid	286·6	269·8	127·0	739·0	866·0	866·0	807·0	290·5	728·0	728·0	619·0
,, oxygen	204·3	193·6	91·0	—	—	269·0	—	97·5	—	—	441·0
,, air	97·0	90·2	43·0	—	27·5	—	25·1·0	—	—	—	—
,, hydrogen	—	—	—	—	—	—	—	—	—	—	—
,, hydrogen solid (30 to 40 m.m.)	21·5	19·7	10·7	55·5	—	—	—	55·0	54·6	—	—
	—	14·4	8·2	—	—	—	—	—	—	—	—
*Calculated Temperatures**—											
B.P. of carbonic acid	—	−77·95°	−78·24°	—	—	—	—	—	—	—	−78·22°§
,, oxygen	−182·20°	−182·67°	−181·52°	—	−182·29°	−183·46°	—	−182·95°	—	—	—
,, air	—	—	—	—	—	—	−189·62°	—	—	—	—
,, hydrogen	−253·03°	−253·37°	−250·35·†‡	−252·81°	—	—	—	—	−252·68°	−252·84°	—
,, hydrogen solid (30 to 40 m.m.)	—	−258·66°	−255·67·†‡	—	—	—	—	—	—	—	—

* No value is attached to the second place of decimals.

† Corrected for oxygen error −251·4°.

‡ Corrected for oxygen error (−252·1°).

§ Dry carbonic acid.

* A Paper read before the Royal Society, February 7, 1901.

case an error in the reading of a low pressure has six times as great an effect as if the initial pressure had been about an atmosphere. If the temperature deduced for the boiling-point of oxygen is corrected, and the same factor of correction applied to the observed liquid hydrogen boiling-point, then it becomes $-251{\cdot}4^{\circ}$.

It is of particular moment to have some estimate of how far errors in the observed quantities employed in Chappuis's formula affect the final value of T.

In the case of an error in t, on differentiating equation (2) we get—

$$dT = T_1 \frac{-x(273+T_1)}{(273+t-xT_1)^2}\, dt \quad . \quad . \quad . \quad . \quad (4).$$

If $x = 1/50$, $t = 13^{\circ}$, $T_1 = -180^{\circ}$; then $dT = 0{\cdot}00339\ dt$, or it would need an alteration of $2\frac{1}{2}^{\circ}$ in t to alter T by 1/100th of a degree at the boiling-point of oxygen. In the same circumstances when $T_1 = -250$, $dT = 0{\cdot}00136\ dt$, so that an alteration of between 7° and 8° in the value of t would only affect the boiling-point of hydrogen by 1/100th of a degree.

From equation (4) the error in T varies with x very nearly. Thus for the second thermometer where $x = 1/115$, a variation of t to the extent of 6° would only affect the boiling-point of oxygen by 1/100th of a degree; and it would require an alteration of 17° in t to affect the boiling-point of hydrogen to the same extent.

In the case of an error in P, a similar process gives—

$$dT = \theta \frac{(\alpha-\delta)P}{(\alpha P_0 - \delta P)^2} \frac{273+t}{273+t-xT_1}\, dP \quad . \quad . \quad (5).$$

If $x = 1/50$, $t = 13^{\circ}$, $P_0 = 760$ m.m., $T_1 = -180^{\circ}$; $dT = 0{\cdot}3563\ dP$, so that an error of 1 m.m. in P would only alter the boiling-point of oxygen by a third of a degree. In the same circumstances at -250°, $dT = 0{\cdot}3516\ dP$, which is practically the same result at the boiling-point of hydrogen as at that of oxygen.

For the second thermometer, these two equations became—

at -180°, $dT = 0{\cdot}3575\ dP$,
at -250°, $dT = 0{\cdot}3548\ dP$.

In each of the last four results if $P_0 = \frac{1}{n} \times 760$ m.m. the formulæ become respectively—

$dT = n \times 0{\cdot}3563\ dP$, and $dT = n \times 0{\cdot}3516\ dP$,
$dT = n \times 0{\cdot}3575\ dP$, and $dT = n \times 0{\cdot}3548\ dP$;

in other words, any error in reading P is magnified in its effect on T directly in proportion as P_0 is diminished. This affords some explanation of the weakness of the results in Experiment No. 3.

In like manner, from an error in P_0, we get—

$$dT = -\frac{P}{P_0}\frac{dT}{dP}\, dP_0 \quad . \quad . \quad . \quad . \quad . \quad (6).$$

Here if $x = 1/50$, $t = 13^{\circ}$, $P_0 = 760$ m.m., $T_1 = -180^{\circ}$;—

$$dT = -0{\cdot}1188\ dP_0,$$

or an error of 1 m.m. in P_0 would only alter the boiling-point of oxygen by a ninth of a degree; but with the same data at -250°, $dT = -0{\cdot}0264\ dP_0$, so that the boiling-point of hydrogen would only be altered by a tenth of a degree for a change of 4 m.m. on an initial pressure of about one atmosphere.

In this case also if $P_0 = \frac{1}{n} \times 760$ m.m. we get similar results to those in the case of P, namely,—

For $x = 1/50$, $dT = -n \times 0{\cdot}1188\ dP_0$ and
$dT = -n \times 0{\cdot}0264\ dP_0$.

For $x = 1/115$, $dT = -n \times 0{\cdot}1192\ dP_0$ and
$dT = -n \times 0{\cdot}0266\ dP_0$.

The general result of an error in either P_0 or P is, that the more reliable experiments are those in which the initial pressure is as high as possible. Hence Nos. 4, 9, 10 are in this respect the most reliable for hydrogen. Also, it is of much more importance that P should be accurate than that P_0 should be so: in fact, for hydrogen an error in P has fourteen times as much effect as the same error in P_0.

We can verify these results from Table I. In Experiment No. 2, where $P_0 = \frac{1}{2} \times 760$ nearly, we have two readings—one at the boiling-point, the other in solid hydrogen—namely, 19·7 m.m. and 14·4 m.m., whose difference is 5·3 m.m. This corresponds to $dT = 3 \times 0{\cdot}3516(-5{\cdot}3)$ degrees, or $5{\cdot}59^{\circ}$. The calculated temperatures for these pressures are $-253{\cdot}37^{\circ}$ and $-258{\cdot}66^{\circ}$, whose difference is $5{\cdot}29^{\circ}$, a satisfactory agreement.

If we compare Experiments Nos. 4 and 9, in both of which the same value of α is used, we can pass from the former to the latter by the formula—

$$dT = -0{\cdot}0266\ dP_0 + 0{\cdot}3548\ dP,$$

in which $dP_0 = -11$ m.m. and $dP = -0{\cdot}5$ m.m., whence $dT = 0{\cdot}152^{\circ}$, the observed result is $-252{\cdot}683^{\circ} + 252{\cdot}806^{\circ}$ or $0{\cdot}123^{\circ}$, which is also satisfactory and explains how so great a drop as 11 m.m. in P_0 has, nevertheless, so slight an effect on the result.

An alteration in the value of x has but little relative effect on the results. As before we have—

$$dT = T_1 \frac{(273+t)(273+T_1)}{(273+t-xT_1)^2}\, dx \quad . \quad . \quad . \quad . \quad (7).$$

If $x = 1/50$, $t = 13^{\circ}$, then—

at $T_1 = -180^{\circ}$, $\quad dT = -57{\cdot}085\ dx$,
at $T_1 = -250^{\circ}$, $\quad dT = -19{\cdot}4205\ dx$,

and for the second thermometer ($x = 1/115$) in like circumstances, and—

$$dT = -57{\cdot}895\ dx.$$
$$dT = -19{\cdot}802\ dx.$$

For instance, if x were altered from 1/50 to 1/80 the result would be to raise the boiling-point of oxygen by $0{\cdot}43^{\circ}$ and that of hydrogen by $0{\cdot}15^{\circ}$.

Finally, the alteration of α for any particular gas, being in any case small, affects the value of T practically only in its main factor T_1. To hundredths of a degree therefore the change in T is inversely proportional to the change in α; or, in other words, is directly proportional to the corresponding absolute zero.

For instance, in Experiment No. 11 had we used the same value of α as for hydrogen the boiling-point of dry CO_2 would have been $-79{\cdot}35^{\circ}$.

Table II. shows what alterations would be required for each of the thermometers, in the values of t, P, P_0, and x to alter the boiling-point of oxygen or that of hydrogen by 1/10 or 1/100 of a degree. The table is calculated for $t = 13^{\circ}$; and in the cases of P and P_0 the initial pressure is taken to be about $1/n$th of an atmosphere.

TABLE II.

		Thermometer No. 1.	Thermometer No. 2.	Alteration of T.
t	at B.P. of O..	$2\frac{1}{2}^{\circ}$	6°	1°
	at B.P. of H..	$7\frac{1}{2}^{\circ}$	17°	$\frac{1}{100}$
P	at B.P. of O..	$\frac{0{\cdot}280}{n}$ m.m.	$\frac{0{\cdot}280}{n}$ m.m.	$\frac{1^{\circ}}{10}$
	at B.P. of H..	$\frac{0{\cdot}285}{n}$ m.m.	$\frac{0{\cdot}282}{n}$ m.m.	
P_0	at B.P. of O..	$\frac{0{\cdot}842}{n}$ m.m.	$\frac{0{\cdot}839}{n}$ m.m.	$\frac{1^{\circ}}{10}$
	at B.P. of H..	$\frac{3{\cdot}79}{n}$ m.m.	$\frac{3{\cdot}76}{n}$ m.m.	
x	at B.P. of O..	0·88 per cent	2·00 per cent	$\frac{1^{\circ}}{100}$
	at B.P. of H..	2·57 "	5·81 "	

Thus, for example, if the initial pressure in either thermometer were about half an atmosphere, an error of 1/7 m.m. in reading P would alter T by a tenth of a degree.

If we take the average values given by these experiments as being the most probable, then the boiling-point of oxygen is $-182{\cdot}5°$, and that of hydrogen is $-252{\cdot}5°$, or $20{\cdot}5°$ absolute. The temperature found for the boiling-point of oxygen agrees with the mean results of Wroblewski, Olszewski, and others. If the boiling-point of oxygen is raised to $-182°$, which is the highest value it can have, then an equal addition to the hydrogen value must follow, making it then $-252°$, or 21° absolute. In a future communication the temperature of solid hydrogen will be discussed.

I am indebted to Mr. J. D. H. Dickson, M.A., of St. Peter's College, Cambridge, for help in the theoretical discussion of the results, and to Mr. Robert Lennox, F.C.S., for able assistance in the conduct of the experiments.

SOME PRINCIPLES AND METHODS OF ROCK ANALYSIS.*

By W. F. HILLEBRAND.

(Continued from p. 102).

V. *Water—Total or Combined* (continued).

Direct Weighing of the Water in Absorption Tubes.

Penfield's Procedure.—The simplest of these methods as to apparatus, and one permitting, by the use of auxiliary arrangements such as are shown and described on page 90, the determination of the hygroscopic as well as any other fraction of the water, is the following glass-tube arrangement (Fig. 6) of Dr. Penfield's (*Amer. Journ. Sci.*, 1894, Series 3, vol. xlviii., p. 37; *Zeit. für Anorg. Chemie.*, 1894, vol. vi., p. 22), whereby the brick and charcoal oven already referred to (Fig. 5), comes again into play, but without the half brick shown in that figure.

The tube is of about 15 m.m. internal diameter, and is fitted with two platinum cylinders at A, one inside, the other outside, where the heat exposure is to be most intense.

These are made from pieces of platinum foil, about 0·07 m.m. in thickness and 8 by 11 c.m. in diameter, which have been previously bent around glass tubes of such a size that when applied to the combustion tubing, the spring of the metal will hold them in place. A large platinum boat, 7 to 8 c.m. long and 11 to 12 m.m. in diameter, with a cross-section like *b*, should be used, since this will readily hold a grm. of mineral mixed with 5 grms. of sodium carbonate. . . . The tube is placed in the angle formed by the charcoal lining, some pieces of charcoal are placed at the sides in front, leaving an opening through which the flame may be directed, and an additional piece is laid on top. The tube can readily be brought to a full white heat, and by forcing a slow current of dry air through the apparatus the carbon dioxide resulting from the decomposition can be removed, and the water carried over into the weighed absorption tube. The glass fuses between the platinum casings, and in a number of experiments that have been tried there has not been a single instance where the glass tube has broken or shown any indication of breaking. After heating the tube will not crack if it is left to cool slowly on the charcoal, but it cannot be used a second time. . . . At the high temperature to which the glass is subjected it of course becomes very soft and the ends must be properly supported; also the rubber connections and absorption apparatus must be carefully screened by asbestos board. By constructing a cover for the boat no material need be lost by spattering, and after making the water determination the contents may be used for the remainder of the analysis.

* *Bulletin of the United States Geological Survey*, No. 176.

The inner cylinder of platinum serves to prevent the glass from collapsing as it softens, whereby distortion of the boat would result, and its withdrawal for further examination of its contents would be impossible.

Gooch's Apparatus.—Of more elaborate apparatus, designed to be used with fluxes, the tubulated platinum crucible invented by Dr. Gooch (*Amer. Chem. Journ.*, 1880, vol. ii., p. 247; CHEM. NEWS, 1880, vol. xlii., p. 326), is capable of affording most excellent service, and it is the one by which far the larger number of water determinations in this laboratory have been made.

Fig. 7, which hardly needs detailed description, shows it in a modified form, which differs from the original forms of Gooch in that the tubes for connecting with both the drying and absorption vessels are constructed wholly of platinum instead of lead glass, the vertical one being bent horizontally at right angles for convenient attachment to the drying towers, and the side one also bent at right angles, but downward, and having its end slightly drawn in at E (Fig 7) so as to admit of easy insertion in the rubber stopper of a U-shaped calcium-chloride tube as shown in Fig. 9. With tubes of the lengths shown in the figure there is absolutely no danger of their ends becoming hot enough by conduction to scorch or soften the rubber stopper or other connection.

The extra first cost of the platinum extension to these tubes over the lead-glass ends of Gooch's original and modified forms need hardly enter as a factor into the question of employment of this apparatus. The glass ends often break, and only a rich lead glass, not easily obtainable, can be used, since it alone will not crack at the joint with the platinum after cooling. In its present form the whole apparatus weighs approximately 88 grms.

As an adjunct to its convenient use there is needed an ordinary upright iron ring stand, with two small sliding rings, and a sliding ring-burner provided with entering ducts for gas and air-blast. Across the uppermost ring there is an arrangement of stout platinum wire (S, Fig. 8), forming at the centre of the ring a secure seat for the upturned flange of the crucible proper. Both rings and burner can be clamped firmly at any height.

The rock powder having been placed in the cylindrical crucible (C, Fig. 7), is there mixed with not more than 3 or 4 grms. of fully dehydrated sodium carbonate,* or more of lead chromate if carbon is to be likewise determined. The crucible is sunk in its seat S (Fig. 8), in the upper ring R' and the tubulated cap T (Fig. 7) is fitted on and attached to the calcium chloride drying towers—preceded by one containing potassium hydroxide if carbon dioxide is likewise to be estimated—on the one side, and to a sulphuric-acid bulb tube B (Fig. 9) on the other. Powdered sodium tungstate—free from arsenic, which would soon ruin the crucible lips—is now poured into the flanged lip L (Fig. 7) in which the cap rests, and a metal vessel of cold water having been raised up by the lower ring R'' (Figs. 8 and 9) until the platinum crucible is sufficiently immersed, the flame of an ordinary blast lamp is turned on to melt the tungstate. As soon as this is fused the flame is removed, and the salt solidifies and makes an air-tight joint, the test of which is the permanence of the column of sulphuric acid in the bulb tubes caused by the contraction of the air in the platinum apparatus as it cools.

After drying by a current of air at 105° C. for two hours, more or less (see below), by means of an air or toluene bath as shown in Fig. 8, the absorption tube A (Fig. 9) is interposed between the sulphuric acid bulbs and the apparatus, being fitted to the latter by its stopper, which is at other times closed by a glass plug, and while a slow current of air continues to pass, the gradual heating and subsequent fusion of the flux is brought about by the

* This has been heated for a length of time to near its fusing point over a free flame or in an air-bath, to decompose the bicarbonate it usually contains, and then placed in a desiccator. Thus heated it is not very hygroscopic. Penfield found that 2·5 grms. of it, spread out on a watch-glass, gained only 0·0002 grm. in fifteen minutes. Potassium carbonate and potassium-sodium carbonate are too hygroscopic by far to be available.

blast-fed sliding ring-burner R''' (Figs. 8 and 9). The sodium-tungstate joint is shielded from the flame by small pieces of asbestos board P (Fig. 9), cut out so as to fit the crucible. When fusion is complete, as shown in the case of sodium-carbonate flux by the decided slackening of the gas current through the safety bulbs attached to the drying tube, the flame is extinguished, and a current of air is allowed to continue until the apparatus is cold.

This apparatus suffers from the drawback of being slightly permeable to combustion gases at high temperature. The defect can be overcome by causing the flame to play upon an outer ordinary platinum crucible, kept permanently filled with sodium-potassium carbonate.

FIG. 6.—TUBE FOR WATER DETERMINATION ACCORDING TO PENFIELD.

A, Outer protecting covering of platinum foil. A second similar foil on the inside prevents the glass from collapsing when heated to softness. *b*, Cross section of platinum boat.

This protective crucible, however, is soon ruined for other purposes, being distorted by the alternate expansion and contraction of the carbonate.

It has been found that if the operation is carried out expeditiously and the final full heat applied for but a few minutes, the error due to penetrating water gases is inappreciable. This hastening may be rendered safer by using rather finely powdered calcium chloride in the central section of the U-shaped absorption tube to avoid large air

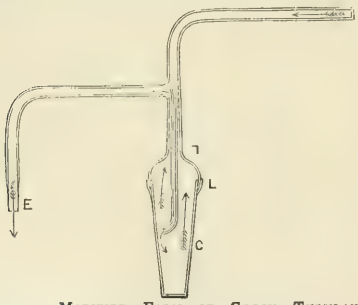


FIG. 7.—MODIFIED FORM OF GOOCH TUBULATED PLATINUM CRUCIBLE FOR THE DETERMINATION OF WATER. (One-fourth natural size. Weight about 88 grms.).

channels. Through this, or any apparatus based on similar principles, the air current should always be forced, not drawn. A warm blast directed upon the exit tube near its entrance into the absorption tube greatly shortens the time required, and is to be recommended.

In this apparatus only the water expelled above 100° to 110° should as a rule be determined, and to effect drying of the mixed mineral powder and sodium carbonate, after luting the tubulated cap on the cylindrical crucible with sodium tungstate, the tube is sunk through a round hole in the cover into a small cylindrical air-bath (Fig. 8), which can be heated from beneath by the same ring burner which is subsequently to fuse the flux. A slow current of air is then forced through, and the drying satisfactorily accomplished.

The reason why it is unsafe to attempt estimation of "hygroscopic" moisture in this apparatus is, that the luting of the two parts must be done by direct application of a flame to the tungstate, and considerable water vapour may enter the apparatus, and be in part retained by the dried sodium carbonate.

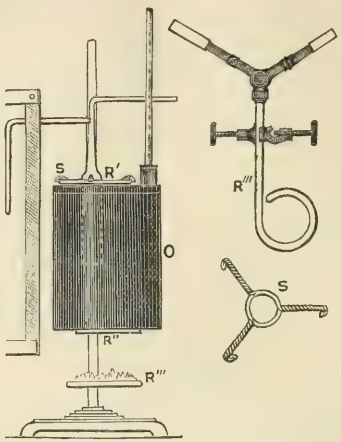


FIG. 8.—DETAILS OF GOOCH CRUCIBLE FOR DETERMINING WATER.

S, Seat of stout platinum wire resting on ring, R', and serving as a support for the crucible; R''', blast-fed ring burner; R'', support for air or toluene bath, O.

Chatard's Apparatus.—The platinum apparatus devised by Dr. Chatard (*Amer. Chem. Journ.*, 1891, vol. xiii., p. 110; *Bull. U. S. Geol. Survey*, 1891, No. 78, p. 84), overcomes the permeability of the metal to gases and affords sharp results, moreover permitting of determining by direct

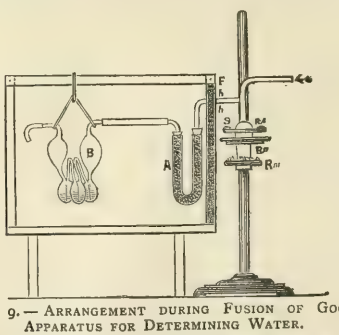


FIG. 9.—ARRANGEMENT DURING FUSION OF GOOCH APPARATUS FOR DETERMINING WATER.

R''', Blast-fed ring burner; F, protective asbestos board shield resting on ring, R''; F F, board forming end of frame and covered with asbestos board to prevent being set on fire by the heat of the blast (this serves at the same time as an efficient shield for the absorption-tube A; in it there is bored a round hole at *h h*, through which passes the outlet tube from the crucible); B, sulphuric acid bulb serving to show the rate of gas current through the absorption-tube and at the same time to prevent back entry of moisture from the air into A.

absorption not only the hygroscopic water, but that which may be driven off at any desired temperature, either with or without fluxes. It is, however, perhaps even more

costly than the Gooch apparatus, and the supposed non-liability to injury by warping, because of the protective layer of borax and asbestos, can hardly be considered as proved.

Merits of the Above Three Forms of Apparatus.—All of these apparatus, except the glass tube of the modified Brush method, permit of the estimation of other constituents besides water in the same portion if necessary, and by the use of lead chromate or potassium chromate, instead of sodium carbonate, graphite, or the carbon of organic matter, can be simultaneously determined with the water.

To one accustomed to its use, and with a drying and suspension attachment permanently set up, the Gooch apparatus, considering its limitations above set forth, offers perhaps the most handy and convenient means for the determination of water in rocks. Its high first cost, in comparison with the glass tube, is fully made up in time by its durability.

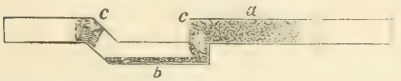


Fig. 10.—Glass Tube for Determination of Water (Jannasch).

b, Mixture of mineral powder with borax; *c c*, plugs of glass-wool; *a*, layer of lead chromate or lead oxide. Total length of the tube, 33 c.m.; inside diameter, 12—14 m.m.

Jannasch's Methods.—This zealous deviser of methods for mineral analysis has published in the *Zeitschrift für Anorganische Chemie* and in the *Berichte der Deutschen Chemischen Gesellschaft* several papers dealing with the problem of water determination in minerals, and in his text-book ("Praktischer Leitfaden der Gewichtsanalyse,") Leipzig, von Veit and Co., 1897), these are collected in more or less modified form.

For the majority of silicates he finds dehydrated borax powder a most efficacious flux, usually at a very moderate temperature. The fusion is accomplished either in a platinum boat, within a glass tube, or in a tube of the form and dimensions shown in the accompanying Fig. 10.

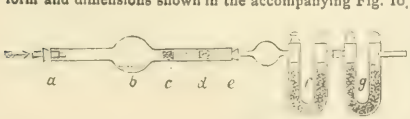


Fig. 11.—Glass Tube for Determination of Water in Special Cases (Jannasch).

Length from *a* to *e*, 26 c.m.; inside diameter, somewhat over 1 c.m.; volume of bulb *b*, 25 c.m.^{3}; *c d*, retaining layer of lead oxide between plugs of glass-wool; *f*, calcium chloride absorption tube; *g*, protective tube.

For rocks or minerals containing not much fluorine a retaining layer of granular lead chromate, or of previously fused and powdered lead oxide, is used as shown at *a*. Plugs of glass-wool are used at *c, c*. Whether or not the boat is employed the borax is first introduced, and, together with the retainer, is thoroughly dried out in an asbestos oven by a hot-air current. Then, after cooling, the mineral powder is added, and thoroughly mixed with the borax. Heat is applied by a flat flame to the mixture, which soon melts and forms a clear fusion, when the action is complete. The blast may be used in extreme cases. The layer of retainer must be kept warm by an auxiliary flame, and the absorption tube must be removed before the glass breaks as soon as this is done. Carbon dioxide can simultaneously be determined by attaching a soda-lime tube to the calcium-chloride tube. For one-half to 1 grm. of silicate Jannasch uses 1½ to 2 grms. of borax.

Regarding the borax method, its inventor insists upon the following points as essential to success, especially when the blast can not be applied:—Most thorough mixing of flux and mineral powder, and a most impalpable fineness of the latter.

The borax itself is prepared by heating pure crystallised borax in a platinum dish till a small portion has melted. That remaining unfused is powdered and again heated in the dish to dull redness for fifteen minutes, with constant stirring. The powder is placed in a tube with tightly fitting glass stopper, and kept over sulphuric acid. It must not be kept long without re-heating, because of being hygroscopic.

Another form of tube used by Jannasch for special purposes is shown in Fig. 11. Minerals, such as topaz, which is not fully decomposed by the borax method, and which contains a large amount of fluorine, are fused at *b* with about six times their weight of lead oxide. A layer of lead oxide between *c d* serves to retain any fluorine escaping from the fusion.

(To be continued).

CONCERNING LIPASE, THE FAT-SPLITTING ENZYME, AND THE REVERSIBILITY OF ITS ACTION.*

By J. H. KASTLE and A. S. LOEVENHART.

(Continued from p. 103).

The Reversibility of the Action of Lipase.

In spite of the vast amount of work which has been done upon the enzymes, we possess at present no unifying conception as to the manner of their action. For the solution of this problem, we must probably look to the study of the kinetics of enzyme action, and one of the first questions to present itself in this connection is: Are the enzymes reversible in their action? If so, then an accumulation of the products of their action should have an increasingly inhibiting effect on the further progress of the change, until finally equilibrium would be established between the initial substance and the products of the change.

O'Sullivan and Thompson (*Journ. Chem. Soc.*, 1890, lvii., 926), in their exhaustive study of the action of invertase on cane-sugar, could not observe any inhibiting effect from the presence of the products of the change. On the other hand, Sheridan Lea (*Journ. of Physiology*, 1890, xi., 226), found the digestion of starch by salivary diastase to be more rapid and much more complete when the products of the digestion were removed by dialysis than when the digestion was performed under identical conditions, but without this precaution. He obtained similar results in his investigation of tryptic digestion. As to the effect of peptone on peptic digestion, the views are somewhat contradictory. Kühne (*Lehrbuch d. Phys. Chemie*, 1866, S. 39), states that peptone has a retarding effect on peptic digestion, while the opinion of Chittenden and Ely (*Journ. of Physiology*, iii., 327), contradicts this. Tamman (*Ztschr. Physiol. Chem.*, 1892, xvi., 271; *Ztschr. Physikal. Chem.*, 1895, xxviii., 426), from his studies of this phase of the problem, arrived at the following conclusions:—

1. Hydrolyses produced by enzymes are incomplete, especially if the quantity of material acted on is large (invertase and rennin are exceptions to this).

2. The incompleteness of the action is due to the accumulation of the products of the fermentation.

3. Removal or dilution of these products, or elevation of the temperature, allows the fermentation to continue.

It would appear that the results obtained by Tamman are easily explicable on the supposition that the enzymes are reversible in their action, the reaction ceasing when

* From the *American Chemical Journal*, xxiv., No. 6

the products of the hydrolysis reach a definite concentration in consequence of equilibrium being established. As Tamman failed to get any indication experimentally that the enzymes are capable of effecting the synthesis of the substances they are capable of hydrolysing, he was forced to explain his results in another way. He advanced the view that the products of the hydrolysis act on the enzyme, transforming it into an inactive modification, and that on removal of these products it is converted into the active modification again.

Oppenheimer ("Die Fermente und ihre Wirkungen," Leipzig, 1900, S. 55), accepting Tamman's results as final, sought to supply a unifying conception of the action of enzymes. He believes the enzymes are capable of inducing only exothermic reactions—that they are only capable of setting free potential energy, and that none of the endothermic, that is, synthetic processes taking place within the organism, can be classed as enzymic, but must be attributed to the peculiar activity of living protoplasm. (The same view has been expressed by Nasse; *Maly's Jahrsbr.*, 1894, S. 718). He admits, however, that this view is completely at variance with the recent work of Hill (*Journ. Chem. Soc.*, 1898, lxxiii., 634), who has proved that the action of maltase on maltose is reversible—first, by showing that maltase can effect the synthesis of maltose from glucose, and, secondly, by showing that the action of maltase on maltose tends to an equilibrium, which is the same whether we start with glucose or an equivalent quantity of maltose.

It is believed that the results reached in this investigation of lipase throw still further light on the subject and greatly strengthen the belief that all enzyme action would probably prove to be reversible if proper conditions of concentration, &c., could be attained.

In many instances, however, it will probably not be practicable to secure the proper conditions, for as in the rennin coagulation of caseinogen solutions, one of the products of cleavage seems to undergo instantaneous rearrangement in the presence of soluble calcium salts, and is thereby removed from the field of activity, thus rendering reversibility impossible. Then again, in some cases, for example, the action of invertase on cane-sugar, the reaction seems to be so nearly complete in one direction that it is doubtful whether reversibility could be demonstrated experimentally. While the catalysis of ethers by strong acids is practically complete, still these are typical reversible reactions. In attempting to determine whether lipase is reversible in its action, it was decided to test its power to effect the synthesis of ethyl butyrate, inasmuch as this substance possesses the following advantages over a true fat:—First, it possesses such a characteristic odour that this alone serves as a very delicate and unmistakable test for its presence. Secondly, in order to effect the synthesis of a fat, it would be necessary, or at least highly desirable, to have the extract of the enzyme free from fat. Up to this time we have not been able to prepare a pancreatic extract free from fat without greatly diminishing its lipolytic power. In the synthesis of ethyl butyrate, however, it would not be necessary to remove the fat, and hence it would be possible to employ the most active pancreatic extract obtainable. Finally, a demonstration of the power of lipase to effect the synthesis of ethyl butyrate would be as conclusive as the synthesis of a fat, for the reason that the compounds are exactly analogous from a chemical point of view.

Experiment 1.—5 c.c. N/100 butyric acid, 2 c.c. of 13 per cent alcohol, and 1 c.c. of diluted glycerin extract of pig pancreas were sealed in a test-tube, and heated at 48·5° for thirty-six hours. When opened it had distinctly the odour of ethyl butyrate.

Experiment 2.—A mixture of 180 c.c. of N/40 butyric acid and 72 c.c. of 30 per cent alcohol was divided into two equal parts. To part 1, 25 c.c. of a 10 per cent glycerin extract of pig pancreas was added; 25 c.c. of the same glycerin extract which had been brought to boiling, and then cooled, was added to part 2. The flasks were left open at ordinary temperature. In a few minutes the flask containing the fresh enzyme had developed a decided odour of ethyl butyrate. The flask was then corked, and allowed to stand a week, when the odour of ethyl butyrate was still perceptible. The flask containing the boiled enzyme was also corked, and was allowed to stand a week under the same conditions. At no time could the odour of ethyl butyrate be detected in the control experiment. Exactly similar experiments were carried out in the presence of toluene water with similar results. Two flasks were also made up, each containing 0·25 grm. of β-naphthol. Here, also, the odour of ethyl butyrate was apparent in the flask containing the active enzyme, while in the flask containing the boiled enzyme there was never the faintest odour of the ethereal salt. Similar results were obtained with glycerin extracts of the cow pancreas. In these experiments, the only test for the production of the ethereal salt was the odour, and although this is very delicate and unmistakable, it seemed desirable to obtain, if possible, larger quantities of the substance. With this in view, the following experiment was made:—

400 grms. of pig pancreas (which had been removed from the animal one and a half hours), was thoroughly ground up with sand and extracted with water, the extract being made up to 2000 c.c. This was divided into two parts of 1000 c.c. each. One part was placed in a balloon flask (A) of 4 litres capacity, while othe other part was boiled for three minutes. After cooling, enough water was added to supply that lost in boiling. It was then placed in a flask (B) similar to (A). To each of these flasks 2 grms. of powdered thymol were added as antiseptic. Each of the flasks was provided with a three-hole rubber stopper, through which passed: 1. A separating funnel; 2, a tube reaching to the bottom of the flask with a small aperture at the end and connected with an apparatus for giving a current of air; and 3, a tube connecting the flask with a condenser. A distilling bulb, with its delivery tube drawn out to a capillary opening, and packed in ice, was used as a receiver. The inner tube of the condenser extended to the bottom of the receiver, and the connection between receiver and condenser was made tight with rubber tubing. 3800 c.c. of practically N/10 butyric acid (5 c.c.=9·2 c.c. N/20 KOH) was made up. This was divided into two equal parts, and to each part was added 100 c.c. of 95 per cent alcohol, and 4 grms. of powdered thymol. One part of this mixture was added to flask (A), and the other simultaneously to flask (B). It was allowed to flow into the flasks very slowly through the separating funnels, four and a half hours being consumed in the operation. The flasks were kept in water-baths at laboratory temperatures 23° to 27°, and both under identical conditions, with respect to sunlight, &c. The initial acidity of the boiled and unboiled extract was the same, viz., 1 c.c.=0·3 c.c. N/20 KOH. The initial activity of the enzyme was taken, and found to be high. In a tube containing 4 c.c. of water, 1 c.c. of extract, 0·26 c.c. ethyl butyrate, and 0·1 c.c. toluene, and heated at 40° C. for fifteen minutes, 6·45 per cent of the ethyl butyrate was hydrolysed. The flasks were allowed to stand forty hours with occasional shaking, both flasks being shaken equally. In order to separate any ethyl butyrate which might have been produced, the flasks were then heated on the water-bath, the distillation being carried on in a slow current of air. About 25 c.c. of the distillate were collected in each case.* The odour of the distillate from flask (A) indicated plainly and unmistakably the presence of ethyl butyrate; it also contained some alcohol and butyric acid, but the odour of these could not be detected on account of the butyric ether. In the distillate from the blank (B), the presence of even a trace of the ether was considered very doubtful by all who examined it, while the odour of alcohol and butyric acid were distinct. The distillate obtained from (A) was re-distilled from a water-bath (this time no

* Previous experiment had shown that on distilling a mixture of ethyl butyrate and a large amount of water practically all the ethereal salt passes over in the first portions of the distillate.

current of air was used), and 5 c.c. of a clear distillate was collected. This was still faintly acid with butyric acid and contained some alcohol.

A small portion of this distillate was reserved for experiment and the remainder was poured into water. The mixture at once became turbid, and a light ethereal oil rose to the surface. Altogether about 1 c.c. of impure ethyl butyrate was obtained in this experiment. Hence about 5 per cent of the butyric acid present had been transformed into the ethereal salt. This quantity was too small for purification, and hence no analysis of it was attempted. Its characteristic odour, however, together with its other properties, and its mode of formation left no room for doubt regarding its composition. A small amount of it was saponified with caustic soda, and the solution evaporated to dryness. On adding sulphuric acid to the residue the odour of butyric acid was perceptible at once.

(To be continued).

THE ACTION OF ALCOHOL AT 95° ON METALS WITH WHICH IT COMES IN CONTACT.

By Dr. MALMÉJAC.

The alcohol used in these experiments was perfectly pure, titrating exactly 95° at a temperature of 15° C., and leaving no residue on evaporation.

Samples of 250 c.c. of this alcohol were placed in flasks of white glass closed with corks, on the 5th of July, 1900; each flask also containing 30 grms. of the following metals:—Copper, iron, tin, lead, zinc, galvanised iron.

For six months these samples were all shaken up at certain periods for the same length of time. On the 5th of January, 1901, we observed at the bottom of the flasks containing the tin, the lead, the zinc, and the galvanised iron a white deposit mixed with the metal, which was itself covered with a sort of cloud of the same colour, and in the flask containing the iron there was a deposit of rust.

With these samples we made the following experiments:—

1st Experiment.

60 c.c. were taken of each, after well shaking. These were evaporated separately on the water-bath in small glass dishes, and the following results were obtained:—

1. Copper	No appreciable residue.
2. Iron	Deposit of rust.
3. Tin	Decided residue.
4. Zinc..	"
5. Lead	"
6. Galvanised iron	"

The cloudiness caused by shaking the solutions (except in the case of the copper), before evaporation, caused us to expect this result.

2nd Experiment.

60 c.c. of each of the filtered liquids were taken. All, except the lead, gave a limpid solution after filtration; the lead solution, even after being filtered several times through double filter-papers, retained a milky appearance.

These various liquids were evaporated on the water-bath in the same way as the former ones, and gave the following results:—

1. Copper	No residue.
2. Iron	Decided residue.
3. Tin	Hardly observable residue.
4. Zinc..	Very decided residue.
5. Lead	Voluminous residue.
6. Galvanised iron	Very decided residue.

On dissolving these different residues in acidulated water, the various metals submitted to the experiment can be detected in the solutions.

It is thus evident that alcohol at 95°, when put in contact with metals for six months, dissolves a small portion of them. This reaction should be, therefore, remembered whenever we have to keep alcohol in metallic receptacles. As the weights of the residues were not determined very accurately we have thought it as well not to publish them. —*Journ de Pharm. et de Chim.*, Series 6, vol. xiii., No 4.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 21st, 1901.

Dr. Armstrong, Vice-President, in the Chair.

Messrs. Hugh Ramage, R. W. Cohen, and A. W. Nunn were formally admitted Fellows of the Society.

The following certificates were read for the first time:—Edward George Paul Bousfield, St. Swithin, Hendon; Albert Ernest Dunstan, 24, Lidfield Road, Stoke Newington, N.; Alfred James Hyder, 22, Gunton Road, Upper Clapton, London, N.E.; William Henry Coutts Jemmett, Tintern, Gap Road, Wimbledon; William Shepperson, Longfield, Gt. Missenden, Bucks; Charles Edmund Shaw Sherratt, 24, Argyll Road, Normacott, Staffs.

It was announced that the following changes in the Officers and Council were proposed by the Council:

As *President*: Professor J. Emerson Reynolds, Sc.D., M.D., F.R.S., *vice* Professor T. E. Thorpe, C.B., Ph.D., D.Sc., LL.D., F.R.S.

As *Vice-Presidents*: Professor Herbert McLeod, F.R.S., and Professor H. A. Miers, M.A., F.R.S., *vice* Professor G. D. Liveing, M.A., F.R.S., and Professor J. M. Thomson, LL.D., F.R.S.

As Ordinary Members of Council: Dr. A. W. Crossley, Professor J. J. Dobbie, M.A., D.Sc., Dr. M. O. Forster, and Mr. S. U. Pickering, M.A., F.R.S., *vice* Professor J. Norman Collie, Ph.D., F.R.S., Mr. Gowland, Mr. C. T. Heycock, M.A., F.R.S., and Dr. Messel.

Mr. F. J. M. Page, Mr. E. W. Voelcker, and Mr. A. C. Chapman were appointed to audit the Society's accounts.

Mr. F. J. Lloyd was appointed to act with the Officers, and Dr. Chattaway, who had been appointed by the Council, in drawing up a Report to the Council on the replies which have been received to the question as to the suggested change in the day and hour of the Ordinary Meetings.

Of the following papers, those marked * were read:—

*20. "*Isomeric Hydrindamine Mandelates and Phenylchloroacethydrindamides.*" By F. S. Kipping and H. Hall.

Although many salts of *d-l*-hydrindamine with different optically active acids have now been submitted to fractional crystallisation (Kipping, *Trans.*, 1900, lxxvii., 861), the resolution of the base into enantiomorphously related compounds has not yet been accomplished; this fact, and the formation in some cases of isomeric salts which appear to be partially racemic, led the authors to try to obtain some direct evidence of the asymmetry of the base.

The fractional crystallisation of *d-l-hydrindamine d-l-mandelate*, $C_9H_{11}N,C_8H_8O_3$, was therefore undertaken in order to ascertain whether the two racemic or externally compensated salts, *d*BdA, *l*BlA, and *d*BlA, *l*BdA, could be separated, but the several fractions proved to be identical, owing possibly to the conversion of one isomeride into the other, *d*BdA,*l*BlA $\rightleftarrows$ *d*BlA,*l*BdA.

From *d-l*-hydrindamine and *d-l*-phenylchloroacetyl chloride, however, two isomeric *phenylchloroacethydrindamides*, $C_6H_5{\cdot}CHCl{\cdot}CO{\cdot}NH{\cdot}C_9H_9$, melting at 150—151° and 124—125° respectively, were obtained; in this case, the isomerides are not mutually convertible in solution, and their formation shows that the base is externally compensated.

d-l-*Hydrindamine* d-*mandelate*, prepared from the pure *d*-acid, is not resolved into different fractions when it is crystallised from alcohol; it is therefore a partially externally compensated salt, *d*Al*B*, *d*A*d*B.

The hydrindamine salts derived from racemic mandelic acid and from pure *d*-mandelic acid respectively are indistinguishable except in optical properties; they both melt at 139—141°, whether heated separately or mixed together in different proportions; they have also the same, or almost the same solubility, for when a mixture of the two is fractionally crystallised, the several deposits have practically the same specific rotations.

It may be concluded therefore that the three optically different compounds, *d*A*d*B, *d*Al*B*, *l*Al*B*, form isomorphous mixtures, and that the salts of the active and inactive acids do not represent true partially racemic or racemic compounds.

The use of externally compensated acid chlorides for the detection of asymmetry, and of the active chlorides for the separation of enantiomorphously related compounds, is being further investigated.

*21. "*Isomeric Benzylhydrindamine Bromocamphorsulphonates and some Salts of* d-l-*Hydrindamine*." By F. S. Kipping and H. Hall.

Benzylhydrindamine, $C_9H_9{\cdot}NH{\cdot}C_7H_7$, prepared by treating *d-l*-hydrindamine with benzyl chloride, unites with α-bromocamphorsulphonic acid, forming a mixture of two isomeric salts, $C_{16}H_{17}N,C_{10}H_{14}BrO{\cdot}SO_3H$, which are separable by fractional crystallisation.

The more sparingly soluble "α-salt" forms transparent plates, melts at 206—207°, and has a specific rotation $[\alpha]_D = +50°$ in ethyl alcohol.

The more readily soluble "β-salt" crystallises in ill-defined prisms, melts at 186—187°, and has a specific rotation $[\alpha]_D = +51{\cdot}5°$ in ethyl alcohol; in chloroform, the specific rotation of the β-salt seems to be slightly greater than that of the isomeride.

Both salts give an optically inactive base when decomposed with barium hydroxide solution, and they both contain an acid optically identical with ordinary *d*-α-bromocamphorsulphonic acid. Since they both contain an asymmetric carbon group, as well as a nitrogen atom which is directly united with (H),(C_9H_9),(C_7H_7), and with the ion of the bromo-acid, they might be regarded as salts of the two different externally compensated bases, $+C+N^v$, $-C-N^v$, and $+C-N^v$, $-C+N^v$, or they may be considered to be analogues of the isomeric hydrindamine bromocamphorsulphonates, &c., which have been recently described (Kipping, *Trans.*, 1900, lxxvii., 861).

d-l-*Hydrindamine* d-*camphorsulphonate*,—
$$C_9H_{11}N,C_{10}H_{15}O{\cdot}SO_3H,$$
prepared from the base and Reychler's camphorsulphonic acid, like the salt obtained with *d*-camphor-π-sulphonic acid, is not resolved into isomerides on fractional crystallisation; it forms long prisms melting at 165—166°, and is very readily soluble in water.

d - l - *Hydrindamine* d - *hydroxy* - cis - π - *camphanate*, $C_9H_{11}N,C_{10}H_{14}O_5$, unlike the corresponding salt of l-*cis*-π-camphanic acid, also remains homogeneous on fractional crystallisation; it forms transparent prisms $(+\frac{1}{2}H_2O)$ melting at 202—203°.

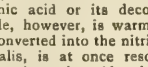
*22. "*Constitution of Bromocamphoric Anhydride and Camphanic Acid.*" By A. Lapworth and W. H. Lenton.

The fact that ordinary bromocamphoric anhydride on treatment with alkalis is in part converted into lauronolic acid by loss of hydrogen bromide and carbon dioxide has led to the view that the bromine atom is in the β position with regard to one of the carboxyl groups (Aschan, *Ber.*, 1894, xxvii., 2112), as it is with β-bromo-acids that this property is almost exclusively associated.

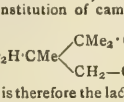
In the belief that the behaviour of the anhydride in this respect is misleading, the authors have made numerous experiments which have resulted in the following observations;—

Camphanic acid, on treatment with phosphorus pentabromide, is re-converted into bromocamphoric anhydride, showing that the lactonic oxygen atom occupies the position of the bromine atom in the anhydride.

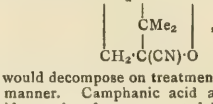
It is difficult to oxidise camphanic acid with any but powerful agents, and when attacked it is usually converted into camphoronic acid or its decomposition products. When its amide, however, is warmed with phosphorus chlorides it is converted into the nitrile, and this, on treatment with alkalis, is at once resolved into hydrogen cyanide and camphononic acid, which, apart from all views as to the constitution of camphor, must have the structure,—



Camphanonitrile is therefore the lactone of an α-hydroxynitrilic acid, namely,—



which would decompose on treatment with alkalis in the above manner. Camphanic acid and bromocamphoric anhydride are therefore represented by the formulæ suggested by Bredt, namely,—



and the formation, from them, of lauronolic acid has not the significance which has been attached to it.

*23. "*The Action of Acetylchloro- and Acetylbromoaminobenzenes on Amines and Phenylhydrazine.*" By F. D. Chattaway and K. J. P. Orton.

In studying the action of nitrogen chlorides and nitrogen bromides on amines and phenylhydrazine, the authors have used the acetylchloro- and acetylbromo-amino-2 : 4-dichlorobenzene recently prepared by them, as these substances are readily obtained pure. The operations have generally been carried out in chloroform solution, avoiding as far as possible the presence of water.

The reaction with the aliphatic amines is represented by the equation—

$$R{\cdot}NH_2 + C_6H_3Cl_2{\cdot}NClAc = R{\cdot}NHCl + C_6H_3Cl_2{\cdot}NHAc.$$

The chloroamino derivatives thus formed can be isolated.

The initial reaction with the aromatic amines (anilines and toluidines) is similar. The halogen, however, immediately wanders from the nitrogen into the para- and ortho-positions if these are unoccupied. When the hydrogen atoms in the positions 2, 4, and 6 are already substituted, no such intramolecular transformation can take place, but the halogen amino-derivatives of such anilines (as *s*-trichloroaniline) are very unstable, and decompose, yielding substituted azobenzenes. The azo-formation takes place to some extent when acetylchloroaminobenzenes react with the less substituted anilines and toluidines.

Two reactions take place between phenylhydrazine and halogen amino-compounds. The one, when phenylhydrazine is in excess, is represented by the equation,—

$$4C_6H_5{\cdot}NH{\cdot}NH_2 + 2(:NX) = = C_6H_5N_3 + C_6H_5NH_2 + 2C_6H_5{\cdot}NH{\cdot}NH_2{\cdot}HCl + 2(:NH);$$

the other, when the halogen amino-compound is in excess, by the equation,—

$$C_6H_5NH{\cdot}NH_2 + 3(:NX) = C_6H_5X + N_2 + X_2 + 3(:NH).$$

In the authors' opinion, the formation of these substances is not a result of oxidation, but depends on the intermediate formation of halogen hydrazino-derivatives.

The following hitherto undescribed substances have been prepared: — *Aceto*-4-*chloromethylanaline*, $C_6H_4Cl{\cdot}NCH_3{\cdot}COCH_3$, m. p. 92°, white plates from petroleum; *o-chloromethylaniline*, $C_6H_4Cl{\cdot}NH{\cdot}CH_3$, a colourless oil, b. p. 218° (760 m.m.); *2-chloro-5-bromoacetanilide*, $C_6H_3ClBr{\cdot}NH{\cdot}COCH_3$, needles, m. p. 141°; 3-*bromo*-4-*chloroacetanilide*, $C_6H_3ClBr{\cdot}NH{\cdot}COCH_3$, rhombs, m. p. 130°; 2:4:6, 2':4':6'-*hexachloroazobenzene*, $C_6H_2Cl_3{\cdot}N{:}N{\cdot}C_6H_2Cl_3$, dark red needles, m. p. 188°.

•24. "*The Preparation of Orthochloroaniline.*" By F. D. Chattaway and K. J. P. Orton.

The authors described a convenient method of preparing orthochloroaniline by the chlorination of acetanilide.

The chlorination is effected by adding the calculated quantity of a strong solution of bleaching powder to a solution of acetanilide (1 part) in glacial acetic acid (3 to 4 parts). Orthochloroacetanilide, which forms from 5 to 8 per cent of the product, is partly separated from the para-derivative by fractional crystallisation from alcohol. The *o*-chloroaniline is finally freed from *p*-chloroaniline by distilling in steam from sulphuric acid.

•25. "*The Bacterial Oxidation of Formates by Nitrates.*" By W. C. C. Pakes and W. H. Jollyman.

In previous communications the authors have described the actions of a group of bacteria upon solutions containing sodium formate, and of another group upon solutions containing sodium or potassium nitrate.

Many of the bacteria which decompose the formate are also found to decompose the nitrate, such, for instance, as the *B. coli communis*, *B. enteritidis* of Gärtner, and the *Pneumobacillus* of Friedländer, each of which converts formic acid into carbon dioxide and hydrogen, and reduces nitric to nitrous acid.

If any of these bacteria be cultivated in a medium containing both formate and nitrate (1 per cent of each), it it will be found that no gas will be evolved. After the lapse of several days, the fluid will be found to contain sodium hydrogen carbonate and sodium nitrite. When the medium contains an excess of sodium formate as compared with the sodium nitrate, gas is evolved which, upon analysis, proves to consist of carbon dioxide and nitrogen.

When the same bacteria are cultivated in media containing *d*-glucose and sodium nitrate, a similar effect is produced, gas is evolved which consists of carbon dioxide and nitrogen, or carbon dioxide, nitrogen, and hydrogen, the latter being found if the sugar is in excess as compared with the nitrate.

The authors have not yet been able to determine whether a similar result would be obtained when the organism used did not act upon both, but they have succeeded in showing that the *B. pyocyaneus* (which does not decompose formate) acts in a medium containing both salts almost as if the formate were absent; they have not as yet been able to find a bacterium which decomposes formate, but which does not reduce nitrates.

26. "*Condensation of Phenols with Esters of the Acetylene Series.* Part IV. *Benzo-γ-pyrone and its Homologues.*" By S. Ruhemann and H. W. Bausor, B.A.

Ruhemann and Stapleton have shown (*Trans.*, 1900, lxxvii., 1184), that phenoxyfumaric acid under the influence of concentrated sulphuric acid condenses to benzo-γ-pyronemonocarboxylic acid, which, on distillation, yields benzo-γ-pyrone. The authors of the present paper have applied these reactions to the cresoxyfumaric acids, and thus obtained the corresponding tolu-γ-pyronecarboxylic acids and tolu-γ-pyrones.

27. "*The Influence of Solvents on the Rotation of Optically Active Compounds.* II. *The Influence of Isobutyl Alcohol and Secondary Octyl Alcohol (Methylhexylcarbinol) on the Rotation of Ethyl Tartrate.*" By T. S. Patterson.

In continuation of work already published (*Trans.*, 1901, lxxix., 167), experiments were described whose object was to determine the influence of *iso*butyl and octyl alcohols as solvents upon the rotation of ethyl tartrate. It was found that both liquids lower the specific rotation of the dissolved active substance, the latter having the greater effect. In both cases, concentrations of distinct minimum rotation occur. This phenomenon was briefly discussed.

It was also shown that ethyl tartrate in *iso*butyl alcohol has a molecular-solution-volume greater than that in *n*-propyl alcohol, but less than that in octyl alcohol, which is in agreement with the generalisation deduced from the results of the former investigation.

28. "*Influence of a Heterocyclic Group on Optical Rotation; the Ethyl and Methyl Salts of Dipyromucyltartaric Acid.*' By P. F. Frankland and F. W. Aston.

The authors have investigated the influence on optical rotation of the heterocyclic furfurane group by preparing diethyl dipyromucyltartrate and determining its rotation. The molecular rotation, $[M]_D\,20° = -321{\cdot}44°$, $[M]_D\,99{\cdot}5° = -266{\cdot}54°$, is, at 20°, intermediate between that of diethyl di-*m*-toluyltartrate ($[M]_D 20° = -306{\cdot}3°$) and diethyl di-*p*-toluyltartrate ($[M]_D\,20° = -484{\cdot}4°$), and at 100° intermediate between that of diethyl dibenzoyltartrate ($[M]_D\,100° = -251{\cdot}6°$) and diethyl di-*m*-toluyltartrate ($[M]_D\,100° = -281{\cdot}7°$). Thus the influence of the pyromucyl radicle is similar to that of the aromatic acid, but unlike that of the fatty acid radicles, the derivatives of ethyl tartrate with two equivalents of the former being strongly lævorotatory, whilst those with the latter are more strongly dextrorotatory than ethyl tartrate itself. The pyromucyl derivative again resembles the corresponding aromatic derivatives in having its lævorotation diminished by rise of temperature, whilst the corresponding derivatives with fatty acid radicles have their dextrorotation increased under the same circumstances.

The authors also described a novel method of continuous automatic esterification which has been advantageously employed by them in the preparation of methyl and ethyl tartrates.

NOTICES OF BOOKS.

Laboratory Instructions in General Chemistry. Arranged by Ernest A. Congdon. Philadelphia. 1901. 100 pp., 8vo. 56 Illustrations. Interleaved.

The author of this book is Professor of Chemistry at the Drexel Institute, Philadelphia, and the "Laboratory Instructions" embody ten years' experience in teaching classes. Much of the material is original; the work can be used in connection with any standard text-book.

The first lessons deal with such simple operations as manipulations with glass-tubing, demonstrations of the differences between physical and chemical changes, and experiments to illustrate divers chemical reactions; then follow easy preparations, as of oxygen, hydrogen, &c., and the usual experiments on metals. The whole course is graded carefully, the instructions are explicit and adequate; moreover, the student is occasionally cautioned against injurious actions.

A valuable feature of the book is found in the appendix of twenty pages containing simple and ingenious experiments for illustrating the laws of the conservation of matter, of definite and multiple proportions, of the influence of temperature and pressure on the volumes of gases, as well as the determinations of molecular weights (by three methods), of equivalent weights, and of atomic weights. Except in this appendix the apparatus required is simple and comparatively inexpensive.

The book is admirably adapted to the needs of beginners, and could be used both with large classes or for home study. It is well illustrated from drawings in the note-book of Mr. D. Owen Hales, a student in the Drexel Institute, and the paper and typography do credit to the publishers, P. Blakiston, Son, and Co. H.C.B.

CORRESPONDENCE.

NUMBERING CRUCIBLES.

To the Editor of the Chemical News.

Sir,—Mr. A. A. Kelly's suggestion (Chemical News, vol. lxxxiii., p. 95), that porcelain crucibles be marked with platinic chloride, was made some time ago in the Chemical News, by Blount, I believe. He scratched the side with a diamond, put on the platinic chloride, lightly wiped away the excess, and ignited.

While admiring the practically indestructible marking in metallic platinum, may I suggest that the crucible be marked with ordinary writing ink and then fired. The letter, number, or approximate weight of the crucible is much more easily made, and stands out distinctly in brown lines for as long a time as such pieces of apparatus usually last.—I am, &c.,

Horace Jervis.

52, Bannon Street, Sheffield.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxii., No. 6, February 11, 1901.

Generation of Hydrocarbides by means of Metallic Carbides.—M. Berthelot.—Metallic carbides can be divided into several groups; their decomposition by means of water or dilute acids giving rise to different hydrogen carbides, such as acetylene, ethylene, formene, and liquid carbides less well known. A study of these metallic carbides and their transformation into hydrocarbides has been rendered more simple by the discovery of acetylides prepared from acetylene, and also by M. Moissan's researches on the production of metallic carbides in the electric furnace. The present paper gives an account of further researches on the thermo-chemical conditions under which hydrogen carbides are generated. The results show that metallic carbides do not, when decomposed by water, give rise to oxides of composition corresponding to that of the carbide.

Observations on the Solution of Solid Metals in Mercury and more generally in other Molten Metals.—M. Berthelot.—Observations made during the reaction of a molten metal, such as mercury, on other metals, show that there exist a number of phenomena resembling those produced during the reaction of water on colloidal bodies, organic or mineral, having the characteristics of emulsions, and which do not tend to confirm the notion of a definite coefficient of solubility.

Formation and Decomposition of Acetals.—Marcel Delépine.—In previous thermo-chemical researches on the acetals of monovalent and plurivalent alcohols, the author stated that the generating reaction ought to be limited by the inverse reaction of water on the acetal formed, $R{-}CHO + 2R'(OH) \gtrless R{-}CH(OR')_2 + H_2O$. The point now considered is that the laws ruling the formation and decomposition of acetals approach in a singular manner the processes of etherification and saponification; or rather that the acetals are the ethers of the corresponding aldehyde, and they behave as a kind of bibasic acid. If their stability with regard to water or alkalis is observed, these substances are seen to resemble ether-oxides, their other properties rendering them comparable with ether-salts.

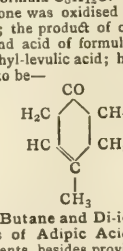
The Elimination of Methane in the Atmosphere.—V. Urbain.—Methane is evolved in abundance from the surface of the earth. Independently of the sources of this gas which exist in all countries, this carbide is a constant product of the fermentation of substances containing cellulose. The author's researches lead him to believe that plants play the same part towards methane that they do towards carbon dioxide. The author proves this by sealing plants hermetically in glass vessels containing about 1300 c.c. of air together with known volumes of methane, and examines the methane undecomposed at the end of definite periods of time.

Action of Ethers of Monobasic Fatty Acids on Mixed Organo-magnesium Compounds.—V. Grignard.—Continuing former researches, the author now examines the action of organo-magnesium compounds on ethers of the monobasic fatty acids, particularly formic and acetic ethers. It is known that organo-zinc compounds, apart from zinc allyl, only react on formic ethers, and then with poor yields. The use of mixed organo-magnesium compounds allows of the simplification and generalisation of a large number of synthetic methods for which formerly organo-zinc compounds were used.

Absorption of Light by Indophenols.—P. Bayrac and C. Camichel.—In no experiment were the authors able to limit the red band found in the absorption-spectrum of the indophenols, at the infra-red side, nor even to observe the culminating point of the curve (the point where the transparence of the solution ceases to increase). They tried also to define the extremities of the band by the condition that the coefficient K has the same very slight value for the two extremities.

Acid and Alcoholic Compounds of Phenylcarbazide with Phenylhydrazine.—P. Cazeneuve.—The acid and alcoholic compounds of phenylcarbazide have been prepared with acids of the fatty series, CH_2O_2, $C_2H_4O_2$, $C_3H_6O_2$, $C_4H_8O_2$, $C_5H_{10}O_2$. The reaction has been made with propionic and normal butyric acid and valerianic acid and valeriane: also with oxalic acid. Crystallised from excess of alcohols, phenylcarbazide of phenylhydrazine gives alcoholic compounds, less stable, however, than the acid combinations; the former being decomposed by the heat of boiling water, and many of them effloresing in the air.

Ketones of Wood Oils: Dimethylcyclohexenone.—A. Béhal.—In a former research the author isolates a series of ketones from wood oil. He now undertakes the separation and examination of another of these ketones. It boils at 194°, its oxime melts at 102·5°, and it gives a benzoyl derivative fusing at 129°. Analysis assigns to it the formula $C_8H_{12}O$. To determine the constitution, the ketone was oxidised by means of permanganate of potash; the product of oxidation giving acetic acid and a second acid of formula $C_6H_{10}O_3$, which was found to be α-methyl-levulic acid; hence the constitutional formula appears to be—



Di-bromated Butane and Di-iodated Butane (1 . 4). New Synthesis of Adipic Acid.—J. Hamonet.—The author's experiments, besides proving the constitution of di-bromated butane and di-iodated butane (1 . 4), furnish a new synthesis of adipic acid.

Nitrate of Uranium.—Œchsner de Coninck.—The author determines the densities of some solutions of uranium nitrate in dilute nitric and sulphuric acid. He then measures the solubility of uranium nitrate in absolutely pure methyl alcohol (prepared from methyl oxalate) in ordinary ether, in ethyl acetate, and in concentrated formic acid.—*Comptes Rendus*, cxxxii., No. 2.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 4th inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Dr. F. H. Anderson, Mr. Alfred Baldwin, M.P., Sir William J. Bell, Mr. R. M. Cocks, Mr. W. Duppa Crotch, Mr. R. S. Dean, Lady Farrer, Major-General Viscount Frankfort de Montmorency, K.C.B., Mr. G. Hartridge, Captain T. B. Heathorn, R.A., Lady Hope, Mr. R. H. Household, Mr. L. S. Little, Mr. F. L. Lucas, Mrs. W. T. Makins, Miss E. M. Marindin, Mr. C. Schiff, and Mr. F. Owen were elected Members. The special thanks of the Members were returned to Mr. Hugh Leonard, F.S.A., for his donation of £100, and to Sir William J. Farrer for his donation of £50, to the Fund for the Promotion of Experimental Research at Low Temperatures.

The Use of Chloride of Lim eas a Purifying Material for Acetylene.—F. B. Ahrens.—Acetylene, purified by passing over materials containing chloride of lime, contains a small quantity of carbonic acid, which, however, causes no inconvenience; but it also contains variable quantities of chlorised organic derivatives, which constitute a source of danger. It also happens that the purifying material (a mixture of sawdust and chloride of lime), may become heated spontaneously and thus become useless. The author has observed that this heating, and consequently the disengagement of chlorine, does not occur when chloride of lime is used alone. He attributes the heating to a reaction between the hypochlorite and the lignine of the sawdust. The temperature attained by the mass depends on the relative proportions of the chloride of lime, water, and sawdust. On mixing 20 grms. of chloride of lime with 10 grms. of sawdust, and 9 c.c. of water, the temperature reaches 130° in seven minutes. The author concludes that sawdust can be replaced by Kieselguhr, powdered coke, brick-dust, or chromate of lead. If sawdust is retained, then a very large proportion should be used with only a small quantity of water.—*Zeits. f. Angew. Chem.*, p. 777.

NOTES AND QUERIES.

** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Arsenic in Coal.—Could any reader give information as regards a good method for the detection and estimation of arsenic in coal?—ANALYST.

MEETINGS FOR THE WEEK.

MONDAY, 11th.—Society of Arts, 8. (Cantor Lectures). "Electric Railways," by Major Philip Cardew, R.E., &c.

TUESDAY, 12th.—Royal Institution, 3. "The Cell as the Unit of Life," by Allan Macfadyen, M.D., B.Sc.

—— Society of Arts, 8. "Some Examples of Romanesque Architecture in North Italy," by Hugh Stannus.

WEDNESDAY, 13th.—Society of Arts, 8. "The Proposed High Speed Electrical 'Monorail' between Liverpool and Manchester," by F. B. Behr, Assoc.Inst.C.E.

THURSDAY, 14th.—Royal Institution, 3. "Greek and Roman Portrait Sculpture," by Prof. Percy Gardner, Litt.D.

—— Society of Arts, 4.30. "The Growth and Trend of Indian Trade—A Forty Years' Survey," by Henry John Tozer, M.A.

FRIDAY, 15th.—Royal Institution, 9. "Through the Heart of Africa from South to North," by Major Alfred St. Hill Gibbons, F.R.G.S.

SATURDAY, 16th.—Royal Institution, 3. "Sound and Vibrations," by the Rt. Hon. Lord Rayleigh, F.R.S., &c.

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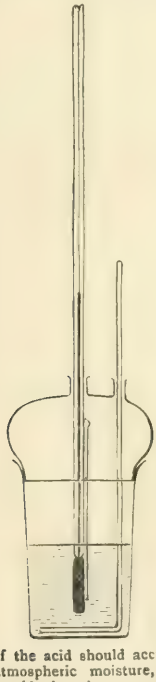
Vol. LXXXIII., No. 2155.

AN IMPROVED MELTING-POINT APPARATUS.

By F. W. STREATFEILD, F.I.C., and J. DAVIES.

In determining the melting-point of organic compounds, which melt at a temperature above 100° C., it is customary to use the well-known apparatus consisting of a thermometer suspended in a beaker of concentrated sulphuric acid, and provided with a glass stirrer.

Certain inconveniences are, however, experienced when employing this somewhat crude arrangement. Some of these are:—1. Annoyance from acid fumes when working at a high temperature. 2. Danger of projection of hot



acid, especially if the acid should accidentally boil. 3. Absorption of atmospheric moisture, and consequent weakening of the acid when the apparatus is not in use.

The drawbacks referred to are avoided by employing the little device shown in the accompanying sketch.

It consists of a light dome-shaped glass cover of such diameter that it rests lightly on the rim or flange of an ordinary narrow beaker. The cover is furnished with two narrow necks, one for the insertion of the thermometer (which is suspended from a retort stand), and the other for the admission of a glass stirrer.

The glass cover is raised by sliding it up the stem of the thermometer, in order to attach the melting-point tube, which is made to adhere to the thermometer by capillarity, induced by moistening the tube and thermometer with sulphuric acid.

It will be found that the cover forms an efficient condenser for the acid fumes, and practically protects the bath from atmospheric moisture.

The apparatus was kindly made for us by Messrs. A. Gallenkamp and Co., of Sun Street, Finsbury, E.C.

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NOTE ON THE ESTIMATION OF HIPPURIC ACID.

By W. A. CATES, A.I.C.

The estimation of hippuric acid in urine can be conveniently effected by the method of Bunge and Schmiedeberg, in which the residue from the evaporated urine is treated successively with absolute alcohol, acetic ether, and petroleum ether. The hippuric acid so obtained is dissolved in hot water, and the solution evaporated to crystallisation. The crystals are transferred to a small weighed filter-paper, dried in the water-oven, and weighed. For every c.c. of the filtrate 0·0015 grm. is added.

The latter part of the process can be considerably shortened if, after the treatment with petroleum ether (which removes benzoic acid, oxy-acids, phenol, and fat), the crystalline residue be taken up in hot water and titrated direct with N/10 NaOH, using phenolphthalein as indicator. The end point is very satisfactory despite the fact that a certain amount of urinary pigment is always extracted along with the hippuric acid, while the results agree well with those obtained by the gravimetric process.

A standard solution of hippuric acid was made by dissolving 0·5 grm. pure hippuric acid in 100 c.c. water on the water-bath; 40 c.c. N/10 NaOH were then added, and, after cooling, the whole was made up to 200 c.c., and the excess of alkali estimated by titration with N/10 HCl, using two drops of 1 per cent phenolphthalein as indicator.

50 c.c. of this solution used 3 c.c. N/10 HCl, showing that 7 c.c. of the N/10 alkali had been used up. Theoretically 6·98 c.c. should have been saturated, reckoning that 1 c.c. of N/10 NaOH corresponds to 0·0179 grm. hippuric acid.

250 c.c. of the urine of a patient who had been taking piperazine quinate yielded:—

Gravimetrically	..	0·1891 grm. hippuric acid
Volumetrically	..	0·1895 ,, ,, ,,

In another case, 200 c.c. of urine ten days old, which had undergone ammoniacal fermentation, and therefore presumably contained but a trace of hippuric acid, was mixed with 50 c.c. (containing 0·125 grm. hippuric acid) of the above standard solution. There was recovered:—

Gravimetrically	..	0·131 grm. hippuric acid
Volumetrically	..	0·1268 ,, ,, ,,

Of the two processes, the volumetric is probably the more accurate, as with most urines sufficient urinary pigment would be extracted to weigh a few m.grms., whereas this would not affect the volumetric estimation.

Hydrocinchonine.—E. Jungfleisch and E. Léger.—A comparison of the two bases, hydrocinchonine and cinchonifine, establishes their identity. The differences apparently revealed at first disappear after a more thorough examination of hydrocinchonine. To procure hydrocinchonine, it is necessary to apply the treatment described in a former paper to cinchonine. In all cinchonines there is a very large proportion of hydrocinchonine, which decidedly modifies the properties of cinchonine itself.—*Comptes Rendus*, cxxxii., No. 7.

THE ESTIMATION OF PHOSPHORUS IN STEEL AND IRON.

By FRED. IBBOTSON and HARRY BREARLEY.

If one may judge from the number of inquiries respecting the estimation of $Am_3PO_4.12MoO_3$ by transforming the molybdenum contents of it into $PbMoO_4$, the operation has been appreciated in the best of all ways; that is, it has been tried.

Shortly after the publication of the method (Chem. News, lxxxii., 55), we were informed that when applied to pig-irons the results were low, and it was suggested that the graphite should not be filtered off until after the oxidation with permanganate. A day or two later we were otherwise informed, that although very satisfactory for steels, "in the case of pig-irons the $PbMoO_4$ method gave results nearly twice as great as the ordinary phosphomolybdate method." With this letter there came four samples of pig-iron, together with the phosphorus percentages as given in the first column of the following table. These had their phosphorus determined in two ways: (1) By filtering off the graphite, and (2) after oxidising with permanganate.

Analysis received. (Long method).	Graphite removed. Before.	After.
0·038	0·034	0·037
0·058	0·056	0·054
0·044	0·045	—
0·049	0·048	0·047

Steels containing 2 to 3 per cent of chromium frequently will not dissolve completely in nitric acid (1·20), even when digested with permanganate. On adding 5 c.c. dilute sulphuric acid (1 to 3) the reaction re-commences after a few seconds with a slight explosion, and is quickly ended. In such cases an additional 2 or 3 c.c. AmHO should be added before precipitating the phosphoric acid. The addition of a little hydrofluoric acid (Chem. News, lxxxii., 269), also clears away the insoluble portion. Perhaps the simplest of all expedients is to dilute the solution which will no longer attack the residue with about its own bulk of hot water; the reaction then re-commences with vigour.

On the few occasions when arsenic has been present in considerable amounts in the steel, and in a few other cases where it has been purposely added, we have not found it to be precipitated along with the phosphorus when the latter was separated rapidly by shaking. This observation has been repeatedly made by advocates of rapid precipitation processes.

There is a considerable demand in large steel-works laboratories for methods by which from twenty to forty estimations of a particular element can be made daily by one person. In relation to this fact, the $PbMoO_4$ process of estimating phosphorus cannot perhaps be considered rapid in comparison with some others, with which, however, we believe it to compare more favourably in point of accuracy. A single estimation to be trustworthy needs at least half-an-hour from the time the drillings are weighed out. A series of results, however, can be obtained in much less time proportionately; for example, thirty estimations have been made in a working day of seven hours by an experienced operator. The ability, however, to deal rapidly with a large number of samples in a systematic and intelligent way is a faculty possessed in greatly different degree by different persons. It also depends very considerably on the peculiar fitness of the apparatus for the operation. Both these considerations are usually overlooked by incredulous persons who think the possibilities of most rapid processes are exaggerated.

The excuse for the following particulars, if they should appear commonplace, is that the desired speed cannot be attained except by attending to them. The reader is supposed to be familiar with the process.

Taylor pattern flasks holding about 300 c.c. are very suitable for use throughout the estimation. The shaking after the addition of the Am_2MoO_4 reagent can be omitted, as each sample will stand at least half-an-hour on the hot plate before its turn comes to be filtered. A smooth funnel $3\frac{1}{4}$ inches in diameter allows the whole of the solution and precipitate to be at once poured on the filter. The flask is washed out twice, and then the filter twice more, each time allowing all the solution to run through. With pulp filters the filtration is very rapid, and the washing particularly effective, since the precipitate and pulp both lie at the throat of the funnel; a wash-bottle having no jet on the delivery tube is used. The yellow precipitate is conveniently dissolved by strong ammonia dropped from a burette. The mixture of ammonium acetate and chloride being kept hot, and the filter being washed with hot water, allows the final precipitation to be made without any further heating. When all are precipitated as lead molybdate the filtration and washing are carried out as before. On each occasion so many filters are used as keep the time fully occupied; more than this invites confusion. The filters are transferred to marked porcelain crucibles, and placed six or eight at a time straight into the hot muffle if needs be. Under this very severe treatment the precipitate never spatters.

It needs little effort to realise that to go through these operations unaided thirty times a day is very hard work. The toil may be lessened in the following manner, but the speed is not increased much, and it is easier for the final precipitate to contain accidental impurities:—After dissolving the yellow precipitate in ammonia and washing the filter, pour the solution at once into 50 c.c. of an acetic acid solution of lead acetate (PbA_2 crystals 8 grms., acetic acid B.P. 400 c.c., all made up to a litre). The white precipitate formed is a mixture corresponding to $Pb_3(PO_4)_2+24PbMoO_4$, and contains 0·644 per cent phosphorus. It is ignited as before, and weighed.

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RADIO-ACTIVE MATERIAL.

By F. GIESEL.

According to the publication in No. 16 of the *Berichte* on "Radio-active Lead and Radio-active Rare Earths," it appears that K. A. Hofmann and E. Strauss are of opinion that they have obtained the above elements absolutely pure, but in the radio-active state.

It is in this connection that I wish to observe that, with the present knowledge of radio-active material, it will be scarcely possible to detect chemically, amongst the metals separated from about 100 grms. of mineral, an impurity so slightly active, which enables them to affect the photographic plate within twenty-four hours. It is therefore not surprising if we find most of the separated products of radio-active minerals, also lead and the rare earths, more or less active.

Commercial uranium salts also show activity, which does not necessarily arise from uranium. Curie would not have succeeded in distinguishing between radium and barium had not tons of pitch-blende of the highest activity been worked up. Even by working on these lines it has not yet proved possible to learn anything with certainty about polonium and actinium.

The active material thus far obtained, not once pure, but only purified, exhibits collectively a far more intense activity than the active metals of Hofmann and Strauss. But radium, for example, would call forth a display of this activity, even when the impurity present lies far beyond the reach of detection by sulphuric acid.

The chief difficulty of separation and detection of radio-active material lies in the generally rare occurrence of minerals of known activity containing uranium and thorium.

Insoluble sulphates, such as those of barium and lead, carry with them very readily active material, as Debierne has demonstrated in the case of actinium, and I myself with uranium nitrate. Consequently, barium radium sulphate frequently contains differently active radium material, which is discovered on purification in the sulphuretted hydrogen and ammonia precipitations. Although this purification was preceded by addition of 2 kg. of radium barium bromide, yet after the radium was practically completely removed by crystallisation, and the barium mostly so, a slight precipitate from the mother-liquor was again obtained with ammonia, which was very strongly active. When the latter was dissolved in hydrochloric acid, and sulphuretted hydrogen passed for some time into the solution, the result obtained was first a yellowish, then a dirty brown precipitate, which when dried weighed 3 m.grms., and was as active as preparations rich in radium. The rare earths, afterwards precipitated as oxalates, had a relatively weak action, but giving forth distinctly the phosphorescent glow.

The presence of polonium appeared to predominate, for the rays exhibited the same high power of absorption and similar characteristics in the magnetic field. This product, after one month, as yet shows no diminution in the intensity of its radiation.

I have now attempted, but in vain, to detect in 2 m.grms. of the substance, bismuth as oxychloride. On the contrary, sulphuric acid produced a precipitate which pointed to lead, but was much less active than the ammonia precipitate which followed next. The filtrate from this, when evaporated, was also active. But, strangely enough, the total action of all the separate products did not amount to the activity of the original 2 m.grms.

Even when greatly enriched products of large quantities of mineral are at one's command, yet, for the reasons given above, chemical tests are useless.

I should further like to mention an observation of Walkhoff, viz., that radium rays cause skin-wounds as do Röntgen rays.

I have applied for two hours to the inner surface of the arm 0·27 grm. of radium-barium-bromide in a double celluloid capsule. At first only a faint redness appeared; after two to three weeks much inflammation was caused, and finally, the outer skin came off, after which it quickly healed.

I noticed a similar action of the rays on living plant leaves; the chlorophyll disappears, and the leaf gradually acquires an autumnal yellow till the colour of the affected spot is brown. This action appears to depend upon molecular re-arrangement which causes a decay in the cell; intense radium rays similarly affect salts, glass, paper &c., the latter becoming brown and brittle.—*Berichte der Deutschen Chemischen Gesellschaft*, 1901, No. 19.

ON CERIUM.

By W. MARCKWALD.

The often repeated statements in present day literature, that cerium consists of at least two elements, have led me to publish herewith a research undertaken by me some time ago with the intention of finally deciding this important question. In this case, as in many other paths, laboratory experiments are superseded by technical methods of working; I will therefore describe the course I adopted, instead of merely stating the results obtained. I started with raw commercial cerium carbonate (50s. per 100 kg.), of which 250 kg., mixed into a paste with water (to avoid frothing over), were dissolved in a just sufficient quantity of raw hydrochloric acid. The heavy metals present were then precipitated by addition of potassium sulphide solution, and from the clear decanted solution in large wooden vessels the cerium was partially precipitated by means of alkaline chloride of lime solution (90 per cent of the required chloride of lime). The deep yellow precipitate was pressed and washed. By going carefully to work this product now contains but little didymium, but relatively much (more than 2 per cent) lanthanum and yttrium. By washing with dilute nitric acid, part of the didymium, &c., was removed. By dissolving in concentrated nitric acid, cerium nitrate is obtained (with evolution of chlorine), from which solution ceriammonium nitrate could be almost quantitatively produced by neutralising with ammonium nitrate. But as the two ceriammonium nitrates crystallise with equal facility, and do not dissociate upon addition of foreign substances, the total solid after being pressed was mixed with hot oxalic acid solution and a little hydrochloric acid, whereupon it is quickly converted into heavy oxalate (with evolution of cabonic acid), from which the remaining impurities, iron, calcium, &c., can be easily removed by washing. The oxalate was treated with great excess of soda, and the washed carbonate dissolved in nitric acid. The completely colourless solution still distinctly showed the absorption bands of didymium in thick films; but not by observation in the eprouvette. This proves that a strongly dispersing system of prisms is not suited to the observation of the absorption spectra, because the weak absorption shadows of dilute solutions are easily overlooked, while a direct vision spectroscope shows the absorption bands in the form of deep black lines, with the advantage of being able to see the whole spectrum simultaneously. One quickly learns to identify the spectrum from the general character of the appearance, without being obliged to measure laboriously the individual lines.

The nitrate solution, treated with ammonium nitrate and evaporated, yielded the salt $Ce_2(NO_3)_6,xNH_4NO_3+Aq$, crystallising in silky shiny needles 20 c.m. long, also the salt $Ce_2(NO_3)_6,3NH_4NO_3,10Aq$, crystallising in large rhombic plates. (Only the latter served for fractional crystallisation).

Both salts are only slightly hygroscopic, and crystallise very easily by the retention of didymium in the mother-liquor. The yttrium earths and lanthanum remain obstinately attached to the salt, a phenomenon which I have also observed upon re-crystallisation of the cerium salt. This double nitrate was now subjected to a systematic fractional crystallisation, and in the course of seven months more than two hundred crystallisations were carried out. Widely removed fractions were tested by Auer's basic method, a part converted into the salt of the dioxide and treated with hot water, but all fractions thus obtained were not in the least distinguishable from cerium preparations which could have been obtained with sufficient care according to the older methods. Also the illuminating power of the incandescent bodies prepared from them was the same. At the same time I may mention that none of the fractions gave a pure white cerium dioxide upon heating; the oxide showed instead a pale yellow glow. Again, the means recommended by Wyrouboff and A. Verneuil for purifying cerium salts gave a cerium nitrate, which upon heating left a yellowish oxide, when reducing mediums were kept away (for which a white heat was necessary). According to this method no preparation free from didymium can be obtained. A little didymium is invariably precipitated with the least basic fractions.

As regard lanthanum and the yttrium elements, these were undoubtedly removed after three crystallisations. In working with compounds containing as much as 4 per cent yttrium, erbium, and above all ytterbium, this method is of no use.

For removal of the latter, the freshly precipitated oxalates are dissolved in strong potash solution (soda is less suitable on account of the less solubility of sodium oxalate). In accordance with published accounts, all the elements of the cerium and yttrium groups dissolve readily in concentrated solutions of the alkaline carbonates. If this solution is poured into a large quantity

of hot water, the carbonates of the elements of the cerium group are precipitated, while those of the yttrium group remain in solution. They can be precipitated as oxalates by acidifying or as hydrates by strong potash, and then further purified by conversion into the sodium double sulphate. (It is incomprehensible why hitherto potassium sulphate, which is eight times as dear, has been used for this purpose). The solubility of the yttrium elements in ammonium carbonate renders it less suitable for the separation. Further, it is necessary by the potassium carbonate method to decant quickly after the deposition of the cerium carbonates if loss is to be avoided.—*Berichte der Deutschen Chemischen Gesellschaft*, 1901, No. 19.

ON THE SEPARATION OF FERRIC CHLORIDE IN AQUEOUS HYDROCHLORIC ACID FROM OTHER METALLIC CHLORIDES BY ETHER.

By FRANK N. SPELLER.

A METHOD for the "Separation of Iron from the Elements by a New Process" was outlined by J. W. Rothe in 1892 (Abstract in CHEMICAL NEWS, vol. lxvi., p. 182), founded on the fact that ferric chloride in aqueous hydrochloric acid solution, when shaken with ether and allowed to settle, remains in the ethereal solution, whereas the other chlorides are almost entirely insoluble, and are retained by the lower aqueous solution.

In endeavouring to apply this method to the analysis of nickel-steel, difficulties were met with, which led the writer to conduct certain experiments to arrive at a better understanding of the conditions under which the separation of ferric chloride takes place.

A solution of ferric chloride containing 0·8 grm. of iron in 100 c.c. HCl (1·193 sp. gr.) was made up. 10 c.c. of this solution was run into a suitable burette, and an excess of ether (20 c.c.) added. The liquids were well shaken together for two or three minutes, then allowed to stand for about thirty minutes until entirely separated at a temperature from 17° to 18° C. A portion of the upper solution was then removed and the iron therein determined.

Similar experiments, varying the specific gravity of the acid, gave the results (calculated to per cent of total iron) shown in Table I.

TABLE I.—*The Deportment of Ferric Chloride with Ether and Aqueous Hydrochloric Acid of the following Strengths.* (*Ferric Chloride contains* 0·8 *grm. Iron in* 100 *c.c.*).

Specific gravity, aqueous hydrochloric.	Per cent of total iron in— Aqueous solution.	Ethereal solution.
1·193	99·0	1·0
1·164	97·5	2·5
1·158	92·84	7·16
1·151	74·0	26·0
1·123	7·2	92·8
1·115	2·4	97·6
1·111	2·0	98·0
1·105	1·95	98·05
1·103	1·95	98·05
1·091	3·3	96·7
1·0825	10·0	90·0
1·069	47·5	52·5
1·06	87·0	13·0
1·0525	98·4	1·6
1·0424	99·6	0·4

Evidently, hydrochloric acid of a specific gravity from 1·100 to 1·115 allows of the most complete separation of iron under the above treatment.

Table II. includes results obtained by varying the quantity of iron in solution and, in some cases, the volume of HCl (1·105) in which the ferric chloride was dissolved. It was ascertained by preliminary experiments that 5 c.c. of ether was necessary for the separation of each decigrm. of iron where the volume of the HCl solution does not exceed 15 c.c.

TABLE II.

Grm. of iron in solution.	Volume aqueous hydrochloric solution.	Residual iron in aqueous solution after shaking with ether.
	C.c.	Grm.
0·08	18	0·00155
0·3	15	0·00151
0·3	20	0·0051
0·3	25	0·0067
0·2	10	0·00204
0·3	10	0·00096
0·5	10	0·00082

In using this principle for the first time in the analysis of copper-nickel mattes, in 1897, it was noticed that considerably more iron was left in aqueous solution when dealing with mattes low in that metal. Sufficient work has not been done to explain the fact, but a concentration (of about 1 grm. of iron in 20 c.c.) appears to be necessary to the most complete extraction.

Nickelous, cobaltous, cupric, manganous, chromic, and aluminium salts in solution in aqueous hydrochloric acid (1·105), when shaken with ether, are insoluble in the ethereal solution. Chromic acid, which may be present with the metallic chlorides, appears to be quite soluble in ether, but is quickly reduced by the latter, and separates in the lower (aqueous) solution a few minutes after shaking.

A volume of 10 c.c. aqueous hydrochloric solution of known strength was shaken in a burette with 15 c.c. of anhydrous ether (re-distilled with $CaCl_2$), and after standing for about thirty minutes at a temperature of 17—18° C., readings at the top of the aqueous and ethereal solutions were taken. The volume of ether in the upper solution subtracted from that originally used gave the apparent solubility, calculated in Table III. to per cent of original volume of aqueous hydrochloric solution.

TABLE III.—*Apparent Solubility of Ether in Aqueous Hydrochloric Acid* per se, *and in the presence of certain Metallic Chlorides. Temperature*, 16—18° *C.*

Spec. grav. Aqueous hydrochloric solution.	Cubic centimetres of ether dissolved by 100 c.c. of— Aqueous HCl *per se*.	Aqueous HCl with Fe_2Cl_6.	Aqueous HCl with $CuCl_2$.	Aqueous HCl with $CoCl_2$.	Aqueous HCl with $NiCl_2$.
1·177	140	139	131	144	107
1·151	—	89	94·2	102·5	83·3
1·140	89	71·5	79·1	—	—
1·131	—	52·8	65·7	72	52
1·123	64	43·3	54	—	—
1·111	—	—	40	—	—
1·115	—	35	—	46	33
1·103	30	26·1	—	33·8	25
1·093	—	21·5	26·5	25·5	21
1·087	—	19·5	—	—	—
1·075	19	16	18·4	—	—
1·063	15·5	13·6	15·6	16·8	14
1·055	14·4	12	14	14	14

Ether, while dissolving 3 per cent of its volume of water, has a very slight affinity for the hydrochloric acid; 10 c.c. of a solution of ether which had been well shaken with an equal volume of aqueous HCl (1·1033) was found to contain only 0·0019 grm. HCl, hence the apparent solubility given in Table III. may be said, with very small error, to have a very simple relation to the real solubility, which it approaches very closely under similar conditions.

In analytical work, the writer has applied this principle in the following manner:—A solution of the chlorides of the metals is obtained to which sufficient concentrated nitric acid is added to completely oxidise the iron present.

It is then evaporated in a 6-oz. wide-necked Erlenmeyer flask on a flat iron plate, the temperature of which can be very easily controlled by rows of small gas jets underneath; this is continued until a thick syrupy consistency is obtained, then taken up with the least possible quantity of hydrochloric acid, 1·105 *specific gravity*.

The solution thus treated is transferred to a suitable separatory cylinder, with a well-ground stopper and tapered out to a rather small orifice below the tap. Ether is added, about 5 c.c. for every decigrm. of iron in solution, and the liquids shaken together for three or four minutes, after which the cylinder is placed in an upright stand. At the expiration of ten minutes, the lower (aqueous) solution may be drawn off; it being quite easy to separate the two liquids to the last drop, owing to the marked contrast in colour.

The residual iron in the aqueous solution should be very small, and in most cases—when in the presence of copper, nickel, and cobalt—may be removed by a single ammonium precipitation, or by adding more ether and again shaking in the same cylinder in which the first separation was performed, when all but a bare trace of iron will be removed.

Most of the above work was carried on from time to time in the Chemical Laboratories of the School of Science, Toronto University, where the interest manifested in the subject by Dr. W. H. Ellis, Professor of Applied Chemistry, gave the writer the advantage of many helpful suggestions.

ON THE DOUBLE CHLORIDES OF URANYL AND THE ALKALINE METALS; AND THE HYDROCHLORATE OF CHLORIDE OF URANYL.

By J. ALOY.

Compounds of Chloride of Uranyl and the Alkaline Chlorides KCl *and* NaCl.

The double chlorides of uranyl and the alkaline metals have up to the present only been prepared in the hydrated state by the evaporation of a suitable mixture of the constituent parts. I have succeeded in obtaining them in the anhydrous state by the direct action of the fumes of the chloride UO_2Cl_2 on the alkaline chlorides.

In a tube of combustion glass arranged over a gas-furnace, I first placed a quantity of non-pyrophoric oxide UO_2, then a series of boats containing the well-dried alkaline chloride; I then passed a current of pure dry chlorine gas through the tube. As soon as the air was completely driven out I heated the part of the tube where the boats were to redness, and gradually extended the heat to the oxide UO_2. The chlorine soon combines with the oxide, which takes a yellow colour on account of the formation of chloride of uranyl; when the transformation is complete the current of gas is increased, and the temperature raised; the fumes of the chloride of uranyl are brought into contact with the alkaline chloride, with which they combine, forming a fusible mass consisting of the double salt.

Chloride of uranyl being very slightly volatile, I was compelled to use a considerable excess of the oxide UO_2 to obtain a definite compound.

The double chlorides of uranyl and the alkaline metals are of a golden-yellow colour; they melt at a red heat without giving off any fumes. They are very soluble in water, and dissolve with considerable ease in aqueous alcohol.

Analysis.—The composition of these double salts was established by determining the weight of UO_2Cl_2 combined with the chlorides, KCl and NaCl, and then estimating the uranium and the total chlorine in aqueous solution.

Double Chloride of Uranyl and Potassium.

	I.	II.
Weight of KCl used	0·622	1·301
Weight of combined UO_2Cl_2; found ..	1·38	2·80
Weight of combined UO_2Cl_2; theoretical for $UO_2Cl_2.2KCl$	1·4	2·9

In 100 parts of material dissolved:—

	Found. I.	Found. II.	Theory.
Uranium as U_3O_8	48·9	48·2	48·7
Chlorine as AgCl	28·3	29·0	28·9

Double Chloride of Uranium and Sodium.

	I.	II.
Weight of NaCl used	0·512	0·601
Weight of combined UO_2Cl_2; found ..	1·44	1·82
Weight of combined UO_2Cl_2; theoretical for $UO_2Cl_2.2NaCl$..	1·5	1·9

In 100 parts of material dissolved:—

	Found. I.	Found. II.	Theory.
Uranium as U_3O_8	51·8	52·0	52·1
Chlorine as AgCl	30·9	31·0	30·8

The above figures correspond with the formulæ $UO_2Cl_2.2KCl$ and $UO_2Cl_2.2NaCl$. The alkaline earthy chlorides do not combine with chloride of uranyl under the same conditions.

Hydrochlorate of Chloride of Uranyl, $UO_2Cl_2.HCl,2H_2O$.—Chloride of uranyl is easily soluble in water, and this solubility is increased by the presence of hydrochloric acid. A saturated hydrochloric solution of this salt, made at 15°, deposits crystals of hydrochlorate of chloride of uranyl when cooled down to −10°.

These crystals are very brillant, and decompose with rapidity, giving off abundant fumes of hydrochloric acid when exposed to the air.

The analysis of this salt is difficult on account of its great instability; to effect it I adopted the method devised by M. Recoura. After forming a fairly large quantity of the hydrochlorate in a test-tube, I added strongly baked kaolin, and then inverted the tube; the salt, thus freed from the mother-liquor, was separated from the kaolin by cutting with a file, and then placed as rapidly as possible in a closed tared glass tube. I then dissolved the substance in water, and estimated the uranium and the chlorine.

I found for 100 parts of material:—

	Found. I.	Found. II.	Found. III.	Theory for $UO_2Cl_2.HCl,2H_2O$.
Uranium as U_3O_8 ..	56·1	56 5	57·0	57·7
Chlorine as AgCl ..	26·5	26·0	—	25·6
Water, by difference	8·8	8·9	—	8·6

These figures correspond to the formula $UO_2Cl_2.HCl.2H_2O$. According to M. Engel's law each molecule of HCl carries two molecules of water.—*Bull. Soc. Chim.*, Series 3, vol. xxv., No. 3.

"The Scottish Electrician."—Electricians are to be congratulated upon the issue of a new journal, *The Scottish Electrician*. Considering the present magnitude of electrical science, it is not surprising that there should be a desire to have a journal of this class published in Edinburgh. For the present it is proposed to issue it monthly, but a more frequent issue is contemplated in the near future if circumstances justify the step. If the high standard of matter that is to be found in the first number is maintained, we predict a very large measure of success for the new venture. The offices of publication are at 37, Queensferry Street, Edinburgh.

CONCERNING LIPASE, THE FAT-SPLITTING ENZYME, AND THE REVERSIBILITY OF ITS ACTION.*

By J. H. KASTLE and A. S. LOEVENHART.

(Concluded from p. 115).

The Reversibility of the Action of Lipase (continued).

THE first distillate from flask (B), viz., that obtained in the control experiment, was treated in exactly the same manner as that from flask (A), *i.e.*, the first distillate was distilled a second time, and the first 5 c.c. of distillate, No. 2, collected. This second distillate had only a trace of the odour of ethyl butyrate, and when poured into water it dissolved without turbidity, and no ethereal oil separated on standing. The conduct of the second distillate from (A) and (B) towards lipase was also tested. Tubes were prepared containing 4 c.c. of water, 1 c.c. of enzyme, 0·1 c.c. toluene, and 0·26 c.c. of the second distillate from (A) or (B).

The following results were obtained :—

With hepatic extract; time, fifteen minutes; temperature, 40° C.

	N/20 KOH required.
	C.c.
(1) 2nd distillate (A)	0·65
(2) ,, ,, (A)	0·70
(1) ,, ,, (B)	None.
(2) ,, ,, (B)	0·05

With pancreatic extract; time, fifty minutes temperature, 40° C.

	N/20 KOH required.
	C.c.
(1) 2nd distillate (A)	0·65
(2) ,, ,, (B)	None.

Control experiments on the second distillate from (A) using the boiled enzyme, showed no hydrolysis even after long standing. These results prove the presence of an ethereal salt in the second distillate from (A), but none, or at best only traces thereof, in the second distillate from (B).

From these experiments it would seem that lipase is reversible in its action upon ethyl butyrate at least.

The fact that lipase is reversible in its action will doubtless afford an explanation of a number of somewhat obscure physiological processes. For example, Schmiedeberg (*Arch. f. Exp. Path. and Pharm*, 1881, xiv., 379), has shown that the kidney of the pig is capable of splitting hippuric acid into benzoic acid and glycocol, and that it is also capable of effecting the synthesis of hippuric acid from these substances. He attributes the splitting of the hippuric acid to a soluble enzyme which he calls histozyme, and which he succeeded in extracting from this organ, and also from the liver. On the other hand, he believes the synthesis of the hippuric acid to be due to the absence of histozyme, and to be induced by some other agency. According to him, the processes of decomposition and synthesis going on in the living organism, are brought about by entirely different agencies. The formation of hippuric acid being a reversible reaction, however, it would seem more probable that the histozyme simply has the power to hasten the establishment of the equilibrium between benzoic acid and glycocoll. According to this view, if benzoic acid and glycocoll are passed through the kidneys, a certain quantity of hippuric acid would be built up under the influence of the histozyme, whereas if hippuric acid itself were passed through this organ a certain quantity of it would be hydrolysed by the histozyme. The fact that lipase can effect the synthesis of an ethereal salt, like ethyl butyrate, will doubtless throw some light on two exceedingly interesting and important physiological processes, viz., the absorption of fats, and the ripening of fruits. Without entering minutely into the physiological aspects of fat-absorption, it may be observed in passing that serious objections have been urged against the various theories which have been put forward from time to time to account for the absorption of fats in the intestinal tract. It has been pointed out by Rachford (*Journ. Physiology*, 1891, xii., 92), that the pancreatic juice is capable of hydrolysing all the fat of a fatty meal in the period of pancreatic digestion. In the living intestine therefore the hydrolysis should be complete, inasmuch as the removal of the products of the hydrolysis by absorption prevents the establishment of equilibrium. On the other hand, the products of the hydrolysis in their transition through the epithelial cells come in contact with a lipolytic enzyme, the presence of which in these cells has been demonstrated in the above (see *ante*, p. 64). The lipase now finds itself in contact with only fatty acid and glycerin, and hence in acting catalytically to bring about the chemical equilibrium, it effects the synthesis of a fat. This would offer a satisfactory explanation of the presence of fat granules in these cells. As the fatty acid and glycerin diffuse out of these cells through the basement membrane, the fat in these cells would speedily disappear were it not that these substances were constantly being absorbed from the lumen of the intestine. When absorption ceases, however, the fat present in the epithelial cells is at once hydrolysed by the lipase present. This hydrolysis is in all probability complete for the reason that the products of the hydrolysis, viz., glycerin and fatty acid, are being constantly removed by diffusion. According to this view, therefore, no fat ever enters or leaves the epithelial cells as such, but as fatty acid and glycerin.

These two substances then enter the central lacteal, where equilibrium is again established, and there is a large production of fat. This view derives support from the fact that fats and soaps exist side by side in the blood (Hoppe Seyler, *Ztschr. Physiol. Chem.*, viii., 503), in the serum of which Hanriot (*Comptes Rendus*, 1896, cxxiii., 753), has demonstrated the presence of a very powerful lipolytic enzyme. It is our intention to look for a lipolytic enzyme in the lymph and lymphatic tissue when the opportunity presents itself.

As is well known, lipase is by no means confined to the animal organism. It has been found by numerous observers in the resting and germinating seeds of various plants, but hitherto it has been looked upon as being concerned solely with the splitting of fats, especially during the period of germination.

On the other hand, Sachs ("Plant Physiology," 1887, p. 347), long ago pointed out that "the presence of fats in the seedling can only be explained by assuming that glycerin and the fatty acids travel from cell to cell, and are continually becoming re-united for the formation of fat," and quite recently Charabot (*Bull. Soc. Chem.*, [3], xxiii., No. 5), has also reached the conclusion that, in the plant, ethereal salts results from the direct action of the free acids on the alcohols. In view of these facts, and of the results described in the above, it would seem logical to conclude that lipase can effect the formation as well as the decomposition of fats and ethereal salts in the plant, and that this ferment plays an important part not only in the utilisation and translocation of these important reserve materials, but also in the storing up of these substances in the seed and fruit.

Summary of Results.

The results reached in this investigation may be briefly summarised as follows :—

1. It has been found that ethyl butyrate is so easily hydrolysed by lipase as to make it a very useful substance in the investigation of a number of problems connected with the chemical action of this enzyme.

2. By means of ethyl butyrate it has been possible to prove the presence of lipase in a number of organs and

* From the *American Chemical Journal*, xxiv., No. 6.

tissues in the animal organism, notably in the liver, stomach, and small intestine.

3. It has been shown that lipase is almost completely removed from its solutions by repeated filtration at ordinary pressure.

4. It has also been shown that lipase is a much more stable enzyme than has hitherto been supposed.

5. It has been shown that animal lipase hydrolyses ethereal salts most rapidly at 40° C., and that at 65° to 70° C. the enzyme is destroyed

6. The conduct of lipase towards a few members of an homologous series of ethereal salts has been studied. It has been found that the stability of these ethereal salts towards lipase decreases with increase in molecular weight of the combined acid. The converse of this was found to be true for the hydrolysis of these ethereal salts by acids.

7. The effect of about twenty of the commoner antiseptics on lipase has been studied. By far the greater number of these substances have been found to exert a harmful effect on the enzyme. This was found to be particularly true of sodium fluoride and hydrofluoric acid and acids generally.

8. A study of the kinetics of the reaction has given the following results :—

First the velocity of the reaction is not proportional to the active mass of the ethereal salt. Secondly, the velocity of the reaction is nearly proportional to the concentration of the enzyme. Thirdly, the reaction is incomplete. This holds for all ordinary concentrations of the enzyme and the ethereal salt. With very concentrated or energetic extracts of the lipase or with very small amounts of ethereal salt the hydrolysis certainly approaches completion. Finally, the coefficient of velocity as calculated according to the equation for a reaction of the first order, is not constant, but shows a regular falling off as the reaction proceeds.

9. By means of lipase we have effected a synthesis of ethyl butyrate from butyric acid and alcohol, thereby proving that the hydrolysis of an ethereal salt as effected by this enzyme is a reversible reaction. Finally, the bearing of this result on fat absorption and the storing up and translocation of fatty reserve material in the plant has been briefly discussed in the above.

SOME PRINCIPLES AND METHODS OF ROCK ANALYSIS.*

By W. F. HILLEBRAND.

(Continued from p. 113).

VI. *Silica, Separation from Alumina, &c.*

Alternative Methods of Decomposition.

Preliminary Remarks.

THE practice of separating alumina, &c., by the usual methods, after first attacking the rock powder by hydrofluoric and sulphuric acids—silica being estimated in a separate portion — while attractive in principle, was abandoned by the writer after fair trial, owing to the disturbance sometimes occasioned by incomplete expulsion of fluorine, and to a less degree by the presence of sulphates instead of chlorides. With exception of the comparatively few analyses made thus, the sodium-carbonate method has always been employed. In the case of rocks rich in fluorine strict accuracy would require the separation of silica to be made as in the Berzelian method for fluorine estimation (see footnote, p. 128), but in practice it is not often necessary to resort to this tedious procedure, since the amount of fluorine is usually small, and it can by no possibility cause a loss of much more than three-fourths its own weight of silica by volatilisation as silicon fluoride when the sodium-carbonate fusion is evaporated directly with hydrochloric acid. Probably the loss is less, since some fluorine perhaps escapes as hydrofluoric acid. However this may be, the error is of comparatively slight importance, since it attaches to the constituent always present in greatest amount.

Various fluxes other than alkali carbonates have been recommended for breaking up silicates insoluble in ordinary acids, such as lead and bismuth oxides, lead carbonate, borax, and boric oxide. Professor Jannasch and his pupils have been especially active of recent years in this line of work, as evidenced by their numerous published papers. One of the advantages these fluxes possess over the alkali carbonates is their removability after serving their purpose, thus allowing the various separations to be made more perfectly and without the annoying interference of several grms. of foreign fixed salts, which are most troublesome in that part of the analysis devoted to the separation of silica, alumina, iron, lime, and magnesia.

Another of their advantages is that with some of them it is possible to estimate in one portion the alkalis, in addition to those constituents usually determined in the silica portion. Where the material is limited, as it so often is in mineral analysis, this is a most important advantage, sufficient to outweigh all possible objections; but in rock analysis, where the supply of material is usually ample, it is rarely worth considering. A still further point in their favour is that it is probably more easy to obtain them entirely free from fixed impurities than an alkali carbonate.

There are, however, objections to their use. With some of them an extraordinary amount of time must be devoted to grinding the mineral to an impalpable powder, and the flux itself may need considerable hand pulverisation. Once introduced, they must be removed before the analysis can be proceeded with, and this removal takes much time and is always a possible source of error.

In mineral analysis these objections are entitled to far less weight than in rock analysis, since the object sought —usually the deduction of a formula—warrants the expenditure of much time and painstaking care. Finally, it has been found that one or more of these fluxes are not available for altogether general use, since certain minerals do not fully succumb to their attack under simple conditions, as andalusite with boric oxide, and others with lead oxide (Jannasch). Therefore however well adapted one or the other of these methods may be for the analysis of homogeneous minerals, it is very improbable that the vivid anticipations of Professor Jannasch, to the effect that the boric-oxide method will soon supersede the alkali-carbonate-fusion method in rock as well as in mineral analysis, will be speedily realised. Nevertheless, the boric-oxide-fusion method, owing to its evident merit, will be described in detail after brief reference to a means of bringing refractory silicates into solution without employing any solid reagent.

Decomposition of Refractory Silicates by Hydrochloric Acid under Pressure.

Jannasch (*Ber. Deutsch. Chem. Gesell.*, 1891, vol. xxiv., 273, and *Zeit. für Anorg. Chem.*, 1894, vol. vi., p. 72), pours upon the finely ground rock powder contained in a platinum tube of about 26 c.m.³ capacity a somewhat diluted hydrochloric acid (4 acid to 1 water), places over the open end a cap which does not hermetically close the tube, inserts the latter in a larger one of potash glass likewise partially filled with the diluted acid, seals the glass tube, and places it in turn in an inclined position in a steel Mannesmann tube containing ether or benzine to equalise the pressure, and heats to any desired temperature up to 400° C.

The chief drawback seems to be a somewhat incomplete decomposition, doubtless due to the necessarily inclined position of the tube, which causes the powder to collect at the lower end, and thus renders decomposition less complete than if the material were spread evenly throughout the length of the tube. Further, the acid

* *Bulletin of the United States Geological Survey*, No. 176.

strongly attacks the platinum unless the air in both the platinum and the glass tubes is replaced by carbon dioxide. Even when this is done, several m.grms. of platinum are found in the silicate solution.

Nevertheless, to those possessing the necessary platinum and steel tubes the method can render efficient service in special cases when economy of material is imperative.

*The Boric Oxide Method of Jannasch and Heidenreich.**

Preparation of the Boric Oxide.—This demands, if the alkalis are to be estimated in the same portion as silica, &c., an absolutely alkali-free boric acid, which can be prepared by two or three re crystallisations of a good commercial article. The purified crystals are dehydrated and fused in a large platinum crucible. This is then suddenly cooled to cause the anhydride to crack into pieces of a size convenient for powdering, which are to be kept in a tight glass and powdered as needed, since the anhydrous oxide is hygroscopic.

Treatment of Easily Decomposable Silicates.—To this flux Jannasch and Heidenreich find that nearly all silicates readily succumb over the ordinary blast-lamp. The fusion is made in a large crucible holding 40—65 c.m.^{3}, and the proportion of flux to be used is gauged according to the nature of the silicate, ranging from 3 to 8 and more parts to 1 of mineral. This last must be finely powdered, especially the most resistant, the authors recommending the expenditure of one-half to one hour's time for the grinding of one-half to 1 grm. of powder. A low burner heat is applied for five to ten minutes till water is expelled, which is then gradually increased till the gas is fully turned on. Bubbling and rising in the crucible is prevented as far as possible by using a short platinum rod which does not reach above the edge of the crucible. When the mass has been in quiet fusion for a time in the covered crucible the blast-flame is applied. The average duration of the entire operation is twenty to thirty minutes, but depends much on the character of the mineral.

Treatment of Refractory Silicates.—For those minerals which, like andalusite, cyanite, and topaz, are not fully decomposable by the heat of the ordinary blast-flame, Jannasch and Weber (*Ber. Deutsch. Chem. Gesell.*, 1899, xxxii., p. 1670), use a flame fed by oxygen instead of air. The blast-lamp, of 2½ m.m. opening, is supplied with gas from at least five or six ordinary gas-cocks, and the flame is made broad and free from luminosity. The mineral having been first heated as above described, but with a much larger proportion of flux—as high as 30 to 1—a few grms. additional of boric oxide are added and the oxygen-blast is applied till, in ten or fifteen minutes, the fusion is as transparent as glass.†

Further Treatment after Fusion.—From this point the further treatment is the same in both cases, and as modified by Jannasch and Weber (*loc. cit.*) is as follows:

The hot crucible is cooled in cold water, and the contents are turned into a very large porcelain or platinum dish, to which, after covering with a glass, a saturated solution of hydrochloric acid gas in methyl alcohol is added.‡ The cover being then removed, the liquid is heated to boiling over asbestos board by an inch-high flame, stirring constantly, or it is left without attention over a lower flame or on a water-bath heated short of boiling. The crucible is cleansed in a similar manner, and its contents are added to the dish. In ten to fifteen minutes, with occasional addition of the methyl chloride, solution is complete, and the liquid is then boiled down to a small volume and evaporated to dryness on the bath. The residue is then digested on a bath at 80° to 85° C. three or four times in succession, with the ether solution, in order to remove the last traces of boron as boric ether. Care should be taken to wash down from the sides of the dish, with methyl-chloride solution, the boric acid formed and deposited thereon during the evaporation.

Possible Objections to the Boric-oxide Method.—Very much is claimed by Jannasch for this method, but with all its undoubted merit there are two points which may militate against it in time. The boric ether, driven off in such enormous quantities, at once decomposes in contact with moisture, and boric acid settles over all objects with which it comes in contact. The hood must become thickly coated. Hence a special hood for these evaporations alone seems to be called for, otherwise boric acid may at any time fall into other dishes, and cause untold trouble. The second objection attaches to the use of the oxygen flame when alkalis are to be estimated in the fusion, and the ability to so determine them is one of Jannasch's chief claims in favour of the method, for it can not be doubted that at the high temperature of this flame alkalis are volatilised in part. Borax can be slowly but wholly volatilised over the ordinary blast, hence there is great reason to fear sufficient loss at this much higher temperature to give rise to serious errors at times.

(To be continued).

* *Zeitschr. fur Anorg. Chem.*, 1896, vol. xii., p. 208.

† An interesting and important observation reported by Jannasch and Weber is that when the oxygen blast has been used for silicates carrying fluorine or mixed with fluorides, the fluorine seems to be wholly expelled as boric fluoride, without loss of silica. If this should prove to be generally true, an easy way is at last afforded for estimating silica in such cases, where even its detection, when present in small amount, has heretofore been difficult.

‡ Made by passing dry HCl into cooled CH_4O for from one to two hours.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, March 8th, 1901.

Dr. R. T. GLAZEBROOK, Foreign Secretary, in the Chair.

A PAPER on "*A Theory of Colloidal Solutions*" was read by Dr. F. G. DONNAN.

Assuming that a colloidal solution is not a true molecular intermixture, but a two-phase system, consisting of exceedingly minute aggregates of the colloid distributed throughout the solvent, the object of the paper was to examine how such a state of affairs might be imagined to come about. By applying the fundamental notions of Laplace's theory of capillary forces to the statical (mechanical) equilibrium at the interface, it was shown that under certain conditions matter in bulk might disintegrate into a homogeneous liquid medium, and yet not attain a state of molecular division, remaining distributed in the form of very thin filaments or sheets whose thickness is comparable with the sphere of molecular attraction. True solution, or molecular intermixture, is regarded, on the other hand, as arising from the kinetic flux of molecules across the interface.

Dr. GLADSTONE said that the study of colloids was one which had been too much neglected. It involves both a knowledge of physics and of chemistry. A colloid is an unstable body, and is always altering its composition. Water of combination is given off on heating, even if the surrounding atmosphere is saturated, and the colloid cannot take up the water again. It is impossible to separate colloids and crystalloids—they merge into one another. The transition forms are not uncommon.

Dr. LEHFELDT asked if it had been proved that colloids have osmotic pressure.

Prof. THRELFALL said that in colloidal solutions some of the substance was not in suspension. Dr. Martin had filled a filter with silicic acid under pressure, and found that it allowed sugar solution to pass through, but stopped colloidal solutions. The author had used opacity as a test for colloids, but silicic acid could be got transparent. There are two kinds of opalescence. One cannot be removed, and exists because the substance is a two-phase system. The other can be removed with difficulty by

filtering, and leaves a transparent substance. The want of transparency should be used cautiously as an argument.

Dr. Donnan, in reply to Dr. Gladstone's remarks on the transition from crystalloids to colloids, said that a substance might be a crystalloid with one medium and a colloid with another. In reply to Dr. Lehfeldt, he said that the only evidence in favour of osmotic pressure of colloids is that colloidal solutions diffuse. He agreed with Prof. Threlfall that opacity should be used carefully as an argument, but stated that his theory referred to a two-phase system.

Mr. Appleyard then exhibited three pieces of apparatus. The first was a slide-wire bridge for measuring conductivities of wires. The slide-wire instead of forming two arms of the bridge forms only one, and the length used is proportional to the conductivity to be measured. If the arm which contains the standard wire used is altered it becomes necessary to alter the divisions of the scale on the slide-wire. This is done by a mechanical arrangement.

The second piece of apparatus was a mechanical gauge for measuring the diameters of spheres. The sphere to be measured is placed between a metal face plate and a piece of glass at the end of the short arm of a pivoted lever. The end of the long arm of the lever moves over a graduated scale, which is calibrated to show directly the diameter of the sphere.

The third piece of apparatus was a galvanometer fitted up for lamp and scale work. The illumination was produced by a 4 volt ¼ candle power lamp, and it was shown that very good results could be obtained from this by using a large condensing lens.

Prof. Threlfall said he had usually used a straight piece of the lamp filament itself, instead of using the lamp in conjunction with a cross-wire.

A paper by Prof. R. W. Wood on "*The Production of a Bright Line Spectrum by Anomalous Dispersion and its Application, the Flash Spectrum*," was postponed until the next meeting at Burlington House, when the subject will be experimentally illustrated by Mr. Watson.

The Society then adjourned until March 22nd, when the meeting will be held in the Chemical Laboratories of University College, London.

NOTICES OF BOOKS.

Arsenical Poisoning in Beer Drinkers. By T. N. Kelynack, M.D., M.R.C.P., and William Kirkby, F.L.S. With 16 Illustrations. London, Paris, and Madrid: Baillière, Tindall, and Cox. 1901. Pp. 125.

The importance of this subject has induced the authors to publish in part their notes on the recent epidemic of arsenical poisoning in Manchester and district; they have therefore given in this volume what they consider to be the more important results of their investigations. These results may be summarised as follows:—(1) That arsenic in quantities sufficient to account for the symptoms complained of was separated from the beer which was actually being consumed by the affected cases; (2) arsenic was found in the secretions of the patients presenting symptoms of arsenical poisoning; (3) arsenic was isolated from the beer received direct from the breweries supplying the local retailers; (4) arsenic was found in varieties of glucose and invert sugar used in the brewing of the very beer in which the arsenic had been detected, and such as was being taken by the affected persons; and (5) arsenic was detected in the tissues of affected cases.

A considerable portion of the book deals with the clinical side of the question, and a number of actual cases are illustrated from photographs of patients, showing pigmentation, dropping of the feet and wrists, transverse ridging of nails, paralysis, wasting, &c.

In the third—or chemical—part of the book, we find a very significant quotation from Dr. A. Wynter Blyth's book ("Foods; Their Composition and Analysis," published in 1896); it runs as follows:—"It is possible for arsenic to be found in beers manufactured from glucose, for in certain kinds of the latter arsenic is occasionally discovered, the substance probably having been introduced by the use of an arsenical sulphuric acid in the process of manufacture." However, the author tells us that, until within the last two months (the preface is dated December 20, 1900), as far as their researches have been carried, no evidence is to be found as to the presence of arsenic in beer.

Part IV. comprises a valuable bibliography of the literature of the subject, and will be of great use to those interested in arsenical poisoning.

In spite of the haste necessitated in compiling this book, owing to the urgency of the matter, the authors are to be congratulated on the excellence of the work they have produced.

The Case Law of the Workman's Compensation Act, 1897. By R. M. Minton-Shenstone, Barrister-at-Law. Second Edition. London: Effingham Wilson; and Sweet and Maxwell. 1900. Pp. 100.

This volume is intended to supplement Part III. of "Accidents to Workmen," which, the author tells us in his preface, has had a very great distinction conferred upon it by being cited and adopted in the Court of Appeal and the House of Lords; this is without precedent for a legal work while in its first edition, and during the lifetime of the author.

The effect of the year's decisions has been briefly summarised, and will be interesting reading for employers of labour. There are also given in the appendices, printed in bold type, the full text of both the Acts dealing with compensation to workmen, viz., the Acts of 1897 and of 1900, in the latter of which the benefits of the former Act were extended to workmen in agriculture.

Analytical Tables for Complex Inorganic Mixtures. Arranged by F. E. Thompson, A.R.C.S. (Lond.), F.C.S.; Teacher of Chemistry at Science and Art Institute, Walsall; Municipal Technical School, Dudley; and Sutton Coldfield Grammar School. Stafford: *Chronicle* Press.

The tables are specially devised for the use of students working for the advanced stage of practical inorganic chemistry of the Board of Education, and will doubtless be found useful to those engaged in preparing students for this and similar examinations. Systematically and clearly arranged, although they do not differ essentially from tables to be found in the majority of text-books, they have the advantage of being in a very convenient form for use, as they are mounted on cloth-lined boards, bound so as to readily open and remain so, and are strong enough to resist the ordinary wear and tear of the laboratory.

The price, 1s. 6d., is moderate enough to bring them within the reach of each individual student.

Dual British and Metric Table Book. By S. Jackson, M.A. (Oxon.), formerly Scholar of Merton College, Oxford, Author of "The Metric System in Theory and Practice." London: Allman and Son, Limited.

The aim of the author of this Table-book is to show, by comparison, the superiority of the metric over the British system of weights and measures. That such a comparison demonstrates this superiority is a question which we do not feel called upon to discuss, but we cannot help thinking that it is injudicious to introduce English terminations to the French terms; the words *liter*, *meter*,

centimeter are not in any way improved by the alteration, while the adoption of *gram* instead of *gramme* is a decided disadvantage, on account of its similarity to grain.

The second part of the book, giving the equivalents of French and English weights and measures, will be found useful to merchants and others unacquainted with the metric system.

We have also received a set of Conversion Tables of Weights and Measures and Foreign Moneys, prepared by the Philadelphia Commercial Museum, 233, South Fourth Street, Philadelphia, in a very compact and handy form, which, though primarily intended for use in the United States, is likely to be found of very general use to the same end. Unfortunately, we again note that the gramme is rendered *gram* and the litre *liter*, &c.

CORRESPONDENCE.

RADIO-ACTIVITY AND ATOMIC WEIGHT.

To the Editor of the Chemical News.

Sir,—The recent researches on radio-active matter seem to indicate that the phenomenon is most marked with elements of high atomic weight; radium, actinium, thorium, and the quite recently discovered radio-active lead, are instances in point. It is, however, very probable that *all* elements are more or less radio-active, but that increase of atomic weight increases the intensity of the action, so that at present our apparatus is only delicate enough to register the heaviest elements.

A glance at Mendeleeff's Periodic Table of the Elements will show the following gradual change with atomic weight of the properties of the elements:—The lightest elements of any series are sharply defined and clear cut in their properties; they effect a condition of chemical repose or equilibrium in one particular state of combination, and this point of maximum stability is quite sharp and definite. In any other state of combination they are unstable.

As, however, the atomic weight increases, this sharpness in combination becomes blurred, and the heavier members of the group often appear to be able to assume with ease more than one state of combination. This shifting and blurring of the point of maximum stability in combination is always apparent with increase of atomic weight in any one group of the Periodic Table.

Now, it is generally accepted that chemical combination is related to presence of ions in the molecules. Thus, *ferrous* iron contains only two *ions*, while *ferric* iron contains three. If we change the iron from the *ferric* state to the ferrous state we lose one *ion*.

Interpreting the above principle in this light, it would appear that an increase in the atomic weight of the elements in any group leads to an increased tendency to change the number of *ions* in the molecule; or, at any rate, it would indicate that *ions* are more easily thrown out and taken in by a heavier atom than by a lighter atom.

Hence, we arrive at the conception of very heavy metals continually casting out into space light ions, until finally their supply runs short or diminishes. If, now, the radio-active metal be treated with another body full of such particles, although the latter body may not of itself throw away many of its ions, nevertheless the heavy element will abstract from it a sufficient quantity to replenish its store, and thus the radio-activity increases again.

The above view indicates the possibility of a connection between readiness of change of valency and radio-activity.—I am, &c.,

Geoffrey Martin.

Bristol, March 2, 1901.

NUMBERING CRUCIBLES.

To the Editor of the Chemical News.

Sir,—Mr. Horace Jervis's suggestion (Chemical News, vol. lxxxiii., p. 118), that porcelain crucibles be marked with ordinary ink and then fired, is very good; but I have found that marking crucibles with an ordinary blue lead pencil (thus obviating the trouble of running ink) and then firing, is better; this produces red lines.—I am, &c.,

W. C. Kriescher.

Villiers Road, Skewen, Neath,
March 11, 1901.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxii., No. 7, February 18, 1901.

Secondary Radio-activity of Metals. — Henri Becquerel.—During the author's experiments on the radio-activity of radium, he noticed the extraordinary power of penetration of a portion of the emitted rays. He has further examined this phenomenon and finds that it is apparently a secondary radiation produced by a further excitement, due to the incident radiation which itself is absorbed; this latter being less penetrating than the original radiation. This appears to be a phenomenon corresponding to that of phosphorescence or fluorescence with regard to light. The penetrability of the secondary radiation, feebler than that of the exciting radiation, is analogous to the same property of the secondary rays derived from the Röntgen rays, which were discovered by M. Sagnac.

A New Gaseous Compound: Sulphuryl Fluoride, SO_2F_2.—H. Moissan and P. Lebeau.—The authors have obtained an apparently gaseous new body belonging to the same series as sulphur hexafluoride. It is very stable, and, on account of its slight affinity for other substances, can be compared to sulphur hexafluoride. Its formula, deduced from its density, analysis, and reactions, is SO_2F_2. It can be considered as a hexafluoride, SF_6, in which a portion of the fluorine is replaced by oxygen. From its formula it apparently corresponds to a known compound —sulphuryl chloride. In reality, the sulphuryl group, if it exists in this new gas, forms part of a much more stable molecule, for which the reactions become more complicated. Once more the experiments described in this paper show that if fluorine is incontestably at the head of the family of halogens, it is a little removed from this group, having special properties and characteristics which separate it from chlorine and bring it at the same time nearer to oxygen.

Alcoylcyanomalonic Ethers and their Derived Alcoylcyanacetic Acids.—A. Haller and G. Blanc.—The authors' researches appear to show that cyanomalonic ether contains a methinic group, CH, and that derivatives are formed bp the substitution of alcoholic radicles for the atom of hydrogen in this group, at least in all the derivatives which were examined; starting from alcoylcyanomalonic ethers, the radicles are joined to the carbon atom in the group CH.

Specific Absorption of X Rays by Metallic Salts.—Alexandre Hébert and Georges Reynaud.—The authors examined a number of chlorides, bromides, iodides, and sulphates of the following metals with regard to their powers of absorbing X rays:—Ammonium, barium, cadmium, calcium, cobalt, copper, lithium, magnesium, manganese, nickel, potassium, sodium, strontium, and zinc. Further observations were made on a series of nitrates

The results obtained show with more certainty, and also more generally than hitherto, that the absorbing power of these substances for X rays increases with the molecular weight. In a compound, it is the element whose atomic weight is the highest which gives to the compound its absorbent properties; this element, moreover, having the power of being electro-positive or electro-negative.

Diphenylcarbodiazine.— P. Cazeneuve.— Diphenylcarbazone is capable of losing two atoms of hydrogen under a very simple oxidising influence, giving diphenylcarbodiazine, a substance hitherto unknown. In order to prepare this body, the author made use of the reaction of silver acetate on phenylhydrazine urea or on diphenylcarbazone.

A New Derived Alcohol of Limonene. — P. Genvresse.—Limonene, under the action of peroxide of nitrogen, gives an alcohol having totally different properties from limonene. This has been called limonenol, and has the formula $C_{10}H_{16}O$. This substance is more difficult to prepare than its isomer, owing to the action of nitrogen peroxide on limonene being much more energetic than on pinene. Limonenol is a secondary alcohol in the same way as pinenol. Treated with the chromic mixture, it gives a ketone—limonenone.

Transformation of Dimethylacrylic Acid into Dimethylpyruvic Acid.—L. Bouveault and A. Wahl.— Ethyl-α-aminodimethylacrylate, $CH_3>C=C(NH_2)-CO_2C_2H_5$, dissolves in dilute cold acids without decomposition, but if the hydrochloric solution is heated to 100° an oily layer separates, whilst crystals of ammonium chloride separate out from the aqueous portion. The decomposition takes place according to the equation $C_7H_{13}NO_2+HCl+H_2O=NH_4Cl+C_7H_{12}O_3$. The new compound is obtained by distillation *in vacuo* of the oily layer after washing with water. This substance boils at 65—69° under 15 m.m. pressure, and possesses a pleasant ethereal odour.

Action of Monohalogen Acids of the Fatty Series on Pyridine and Quinoline.—L. J. Simon and L. Dubreuil.—In general, the reaction of the monohalogen acids of the fatty series on pyridine or quinoline depends on the relative proportions of the acid and the base. If two molecules of base to one of acid are employed, the reaction gives a basic chlorohydrate almost quantitatively,

$$2(R{-}CHBr{-}CO_2H)+3R'N+H_2O=$$
$$=\left(\begin{array}{c}R{-}CH{-}CO\\ |\qquad\quad|\\ R'{-}N{-}O\end{array}\right)_2 HBr.H_2O+R'NHBr.$$

When the quantity of tertiary base diminishes, as when equimolecular quantities are employed, the quantity of basic bromohydrate diminishes, while a neutral bromohydrate appears whose constants of solubility are quite different.

Pyrogallolsulphonic Acids. — Marcel Delage. — Pyrogalloldisulphonic acid is prepared by the action of fuming sulphuric acid on pyrogallol, and analysis shows it to have the formula—

$$C_6H(OH)_2(OH)(SO_3H)_2+4H_2O.$$

The author prepares the barium and calcium salts of this acid.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxiii., Nos. 18 and 19.

This number contains no original chemical matter of interest.

Nos. 20 and 21.

Action of Hydrogen on Sulphides of Arsenic.—H. Pélabon.—Already noticed.

Selenides of Iron.— M. Fonzes-Diacon.— Already noticed.

General Method for the Preparation of the Mixed Carbonic Ethers of the Phenols and Alcohols.—E. Barral.—Already noticed.

Some Mixed Carbonates of Pentachlorophenol and Alcohols.—E. Barral.—Already noticed.

Some Pentachlorophenates. — L. Jambon. — The author has prepared a number of pentachlorophenates by the two following methods:—(1) By boiling finely-ground pentachlorophenol for about an hour, with a base such as ammonia, a solution of soda, potash, or baryta, &c. The boiling solution is filtered, allowed to crystallise, and the crystals collected and drained very quickly, as they absorb carbonic acid from the air. In this manner the pentachlorophenates of lithium, ammonium, strontium, barium, sodium, potassium, calcium, and aniline were prepared. (2) By the double decomposition of an alkaline pentachlorophenate and a soluble salt; this is a convenient method for preparing those which are insoluble, or nearly so, in water; but by this method it is necessary to operate in a warm, *absolutely neutral* solution; otherwise, if the solution is alkaline, insoluble pentachlorophenates, containing equally insoluble oxides, may be formed, or, if the solution is acid, there will be an excess of pentachlorophenol. The author then goes on to describe the properties and composition of a large number of these bodies.

Some Iodised Derivatives of Methylphenylketone. —A. Collet.—These bodies were obtained by heating on a water-bath to about 60—70° an alcoholic solution of chlorised or bromised ketones with a slight excess of iodised potassium in a fine powder, with frequent stirring. The warm liquid is filtered to remove the chloride or bromide of potassium formed; the iodised ketone is deposited on cooling in more or less yellowish crystals. One or two re-crystallisations in boiling alcohol, especially in the presence of animal black, suffices to purify the product. The author then describes the bodies obtained.

The Acidimetric Estimation of Protocatechuic Acid.—H. Imbert.—0·1725 grm. of the acid, dried at 105°, was dissolved in 50—100 c.c. of warm water. On cooling, the liquid was titrated with a 5·6 per cent solution of potash. 11·7 c.c. of this solution were required, which, supposing the acid to be monobasic, would indicate the presence of 0·180 grm. of acid; or, in other words, one molecule of the acid requires 1·04 molecules, and not 1·5 molecules of potash. The same operation was repeated with soda, and one molecule of the acid required 1·05 molecules of alkali. The reddish violet colour produced on adding 1·5 molecules of the base must not be taken as the end of the reaction in the presence of phthalein. The true end of the reaction is found by touching a drop of the solution, on a white tile, with a drop of an alcoholic solution of the indicating reagent; in this manner the faintest rose tint can be observed.

The Nitration of *m*-Chlorotoluene.—F. Reverdin and P. Crépieux.—By digesting *m*-chlorotoluene at the ordinary temperature with nitric acid of 1·52 density, a mixture of mononitrated derivatives is obtained. If the nitration is performed in the presence of sulphuric acid, a dinitrated derivative is formed, viz., chlorodinitrotoluene; this body crystallises in beautiful needles of a pale yellow colour; it is fusible at 91°. By partial reduction, by passing a current of sulphurous acid through its alcoholic solution treated with ammonia, a chloronitroamidotoluene is formed, $C_6H_2CH_3.Cl.NO_2.NH_2$, which crystallises in a mixture of ligroin and benzene in yellow flakes, fusible at 120°; by complete reduction, a chlorotoluylenediamine is formed, fusing at 123°.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Lime in Manuring.—Could any of your readers inform me if crushed limestone could be used as a substitute for lime in manuring. —X.

Arsenic in Coal.—(Reply to "Analyst").—As the arsenic in coal will exist as sulphide, it will be necessary to proceed as follows:—Mix the finely-powdered coal with strong nitric acid and evaporate to dryness on the water-bath; the residue is treated with water and evaporated to dryness; this is repeated. The residue should then be evaporated to dryness with dilute sulphurous acid, mixed with water, and again evaporated to dryness. The sample, after being prepared in the above manner, should be examined by Gutzeit's test (lead acetate modification). This is the best method for the quantitative determination of minute traces of arsenic —E. D.

MEETINGS FOR THE WEEK.

MONDAY, 18th.—Society of Arts, 8. (Cantor Lectures). "Electric Railways," by Major Philip Cardew, R.E., &c.

TUESDAY, 19th.—Royal Institution, 3. "The Cell as the Unit of Life," by Allan Macfadyen, M.D., B.Sc.

—— Mineralogical, 8. (This meeting will be held in the Apartments of the Geological Society, Burlington House). "Notes on an Occurrence of Minerals at Haddam Neck, Connecticut, U.S.A.," by H. L. Bowman, M.A., F.C.S. "On Calaverite from the Cripple Creek District," by G. F. Herbert Smith, B.A. (with Chemical Analysis by G. T. Prior, M.A., F.G.S.). "On the Arrangement of the Chemical Atoms in Boracite and Cassiterite," by W. Barlow, F.G.S.

WEDNESDAY, 20th.—Society of Arts, 8. "Evolution of Form in English Silver Plate," by Percy T. Macquoid.

—— Microscopical, 8. A Demonstration on the Metallography of Iron and Steel (with Lantern Illustrations), by Wm. H. Merrett, Assoc.R.S.M., F.C.S.

—— Institution of Mining and Metallurgy, 8. (Annual General Meeting). "The Electric Power Station at the Pierrefitte Mine," by E. H. Davies. "Note on Smelting Lead-copper Ore" and "Note on Lead Assaying," by P. R. Robert.

THURSDAY, 21st.—Chemical, 8. "Researches on Morphine" (Part II.), by S. B. Schryver and F. H. Lees. "The Constitution of Pilocarpine" (Part II.), by H. A. D. Jowett. "Note on the Latent Heats of Evaporation of Liquids," by Holland Crompton. "Action of Dry Silver Oxide and Ethyl Iodide on Benzoylacetic Ester, Desoxybenzoin, and Benzyl Cyanide," and "Alkylation of Acylarylamines," by G. D. Lander.

—— Royal Institution, 3. "Shakespeare in Relation to His Contemporaries in Art," by Sir Wyke Bayliss, F.S.A.

FRIDAY, 22nd.—Physical, 5. (This Meeting will be held in the Chemical Lecture Theatre of University College). "On the Expansion of Silica," by Prof. Callendar, F.R.S. "The Spectroscopic Apparatus at University College," by Dr. E. C. C. Baly.

—— Royal Institution, 9. "Some Recent Work on Diffusion," by Horace T. Brown, LL.D., F.R.S.

SATURDAY, 23rd.—Royal Institution, 3. "Sound and Vibrations," by the Rt. Hon. Lord Rayleigh, F.R.S., &c.

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MICHAELMAS TERM.—Monday, October 1, to Saturday, December 15.
LENT TERM.—Monday, January 7, to Saturday, March 30.
EASTER TERM.—Monday, April 22, to Saturday, July 27.

Forms of application can be had from the Assistant Secretary, Royal Institution, Albemarle Street, W.

TECHNOLOGICAL EXAMINATIONS, 1901.

CITY AND GUILDS OF LONDON INSTITUTE.

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Only in exceptional cases and by payment of an additional fee can applications be received from Local Secretaries after that date.

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THE CHEMICAL NEWS.

Vol. LXXXIII., No. 2156

NOTES ON THE SPARK SPECTRUM OF SILICON AS RENDERED BY SILICATES.*

By W. N. HARTLEY, F.R.S.

The interesting account by Mr. Lunt (*Roy. Soc. Proc.*, vol. lxvi., p. 44), of his identification of three lines of silicon, corresponding with three unknown lines in the spectra of certain fixed stars, contains the following remarks :—

"It is a curious fact that Hartley and Adeney, and Eder and Valenta, who alone give us any extended list of lines due to silicon, appear not to have examined the spectrum of this element in the region of the three rays here considered. Their published wave-lengths show only lines in the extreme ultra-violet, and the majority of them are quite outside the region which can be examined by the McClean star spectroscope."

There is an inaccuracy here, and a similar mistake as to authorship occurs in the paper of Eder and Valenta. Silicon was not one of the sixteen elements whose spark spectra were investigated by Hartley and Adeney (*Phil. Trans.*, 1884, Part I., p. 63), because it was found to be practically a non-conductor, of electricity, and no uninterrupted stream of sparks could be obtained from it. A prior publication (*Roy. Soc. Proc.*, 1883, vol. xxxv., p. 301), "On Line Spectra of Boron and Silicon," by me, gives descriptions and wave-lengths of lines characteristic of these elements which were observed in solutions of borates and silicates. (For a list of these lines, see also Watts's "Index of Spectra," p. 127, 1899. In Appendix E., p. 21 of the Index, the same list of lines is headed H. and A., which is erroneous).

Having some of the spectra photographed in 1883, I find upon examination of the plates that they were closely investigated at that time. They show no trace of any line of silicon less refrangible than 2881·0 (Angström's unit).

There is a line at the less refrangible extremity of the spectrum which, to judge from its position, is yellow or yellowish-green in colour; but it certainly does not belong to silicon, because solutions of a silicate, and of hydrofluosilic acid containing 1 per cent, 0·1 per cent, 0·01 per cent, and 0·001 per cent of silicon, show this line to be stronger in the spectrum given by 0·01 per cent than in any other of the photographs. It has every appearance of, and no doubt is, the well-known pair of sodium lines with a mean wave-length of 5893. A concentrated solution of sodium silicate gave no stronger indication of this line, and only a feeble representation of the strongest sodium line 3301. This may be accounted for by the remarkable fact referred to in the original paper, that the lines of the metal in borates and silicates seem to be suppressed when the spectra of boron and silicon appear with greatest intensity, but if the quantity of the borate or silicate in the solution is diminished, the sodium lines gain in strength.

There is, however, a line near a very strong air line seen in the spectrum of a 1 per cent solution. It continues to increase in length and intensity in other spectra as the proportion of silica diminishes; otherwise it would not be noticeable because it is extremely short, feeble, and enveloped in air-lines when photographed from a 1 per cent solution. A solution equivalent to 0·001 per cent of silicon yields a spectrum in which this line is about one-fourth of the length of the air-lines, and of the seven carbon lines in other parts of the spectrum.

* A Paper read before the Royal Society, February 21, 1901.

It is in fact the least refrangible carbon line from the graphite electrodes 4266·3 (Hartley and Adeney), and is visible and of normal strength and length on photograph No. 10 in the *Journal of the Chemical Society*, 1882, vol. xli., p. 90. It is one of those lines which is occasionally absent from the carbon spectrum, and it is somewhat lengthened when the electrodes are wet (*Phil. Trans.*, 1884, Part I., p. 49). It is doubtless a carbon line, for Deslandres (*Comptes Rendus*, 1895, vol. cxx., p. 1259), gives its wave-length as 4267 (Rowland's unit), and he used carbon purified in Moissan's electric furnace. The least refrangible of the silicon lines on my plates is at wave-length 2881·0, and it corresponds with a line in the arc spectrum 2881·1 (Liveing and Dewar).

There is a group of air-lines* 4446·02, 4432·58, 4425·90, 4415·51, and 4413·60, then comes 4628·95 and 4674·2, but there is no trace of any silicon lines between 4573 and 4553 where Mr. Lunt found three.

Mr. Lunt used a powerfully disruptive discharge, and that apparently is sufficient to account for the difference in the spectrum which he obtained. I have always employed very simple apparatus, but it happens that when investigating the coefficient of extinction of the various rays of silicon a second series of experiments was made with a more powerful coil and jar. It was found that when all the lines had become very short, and the weaker lines had nearly disappeared, they could be reproduced to a great extent from the same solution by increasing the capacity of the Leyden jar or condenser; but as only extremely dilute solutions of silicates were used, the lines obtained by Mr. Lunt from the solid silicates did not appear.

I give here the normal length of the six lines in the characteristic group as they are seen when a 1 per cent solution and graphite electrodes are used, and of two isolated lines which are less refrangible; with them are compared the lines photographed from other more dilute solutions. The sodium line λ 3301 appears as a long line in the 1 per cent solution, and becomes shorter as the quantity of substance is reduced.

Silicon Lines.

A. Strength of solution, or per cent of silicon.
B. Length of the lines in hundredths of an inch.

Description of lines.	Wave-lengths. (Rowland's unit).	A, 1·0. B.	A, 0·1. B.	A, 0·01. B.	A, 0·001. B.
Strongest but one of the group	2506·8	20	10	10·0	9
A weaker line.. ..	2514·0	20	12	10·0	8
Strongest and longest	2515·9	20	15	10·0	10
The weakest lines of the group	2518·9	20	9	7·5	7
	2523·9	20	10	7·5	7
	2528·6	20	10	7·5	7
An isolated line weak and thin	2631·8	17	6	2·0	Barely visible
Very strong line ..	2881·5	22	14	10·0	9

Observations were carried as far as a solution containing 0·00001 per cent of silicon, the two strongest lines being still visible, but as the photographs of these more dilute solutions have been damaged by being kept so long a time in the atmosphere of the chemical laboratory they not now available for similar measurements.

As the sodium lines are suppressed when the silicon lines are strong, the two carbon lines are also reduced very much in length and strength. This is very easily observed on account of the close proximity of the silicon lines, the wave-lengths of the two carbon lines being 2508·7 and 2511·6 (Hartley and Adeney). In the more dilute solution,

* These wave-lengths are copied from the original numbers written upon the 36-inch enlargements of the spectra referred to as being published in the *Journal of the Chemical Society*. The values are according to Angström's unit, and are doubtless not so accurate as numbers more recently determined.

these lines are observed to be lengthened until they become of the normal dimensions of 20/100ths of an inch. It thus appears more than probable that the suppression of the sodium does not result from any chemical action within the spark discharge such as might be supposed to occur if the sodium were dissociated from the compound, and being in contact with a silicate were to liberate silicon, or to combine with silicon directly, and in presence of water give rise to the formation of silicon hydride.

The suppression of much of the sodium spectrum, and the shortening and weakening of the carbon lines, is more likely to be a purely physical phenomenon than the result of any chemical reaction in the spark.

ON SOME PROPERTIES OF LIQUID CHLORINE.

By A. LANGE.

Following on my researches on liquid ammonia and sulphurous acid (*Zeit. p. die ges. Kältenidus*, 1898, p. 39; *Journ. Soc. Chem. Ind.*, 1898, 191; *Zeit. f. Angewandte Chemie*, 1899), I have determined the specific gravity of liquid chlorine. These determinations are of special interest, as Knietsch (*Liebig's Annalen der Chemie*, cclix., 10) has also worked on this subject, and has given the specific gravity of chlorine between −80° and +80°; his figures may therefore serve as a check on the correctness of the method I have adopted.

At temperatures below 36°, Knietsch determined the densities in the usual manner, by estimating the volumes occupied at different temperatures by the same volume of liquid in a calibrated tube, taking into account the gaseous residue; at 40°, he placed a sensitive areometer in the liquid chlorine contained in a larger tube, and read the density directly. The first method enables the reading to be made correctly to the third place of decimals; the second method is less exact in spite of the compensation caused by the increase of volume of the areometer due to the elevation of temperature and the diminution of this volume due to the increase of pressure. With this second method, it is hardly possible to guarantee the correctness of the second decimal in the figure representing the density.

I will now describe briefly the principle of the method of determination I have adopted:—A vessel, of which the volume is exactly known, is filled with a given weight of a liquefied gas. By applying heat, the liquid dilates and finally fills the vessel. This point once reached, the rise of temperature, which has till now been slow, becomes notably quicker. Knowing the temperature produced by the sudden increase of pressure, we can deduce, with the help of other data, the density of the gas liquefied at this temperature. At low temperatures I used the following method, which, however, is a little less exact:—A vessel filled at a very low temperature was gently heated to the desired point, and the excess of liquid was allowed to pass into a second receiver, in which a higher pressure was maintained than in the first. For details of the operation I must refer my readers to my papers on ammonia and sulphurous acid; I would only remark here, that in the determinations of the specific gravity of liquid chlorine by the method giving the greatest variations of pressure, although care may be taken to drive all the air out of the tube of the manometer by introducing a little liquid chlorine, there is always an oscillation of the pointer of the manometer of about 0·5 atmosphere at about 1° before the temperature finally observed; this oscillation then gradually diminishes, the pointer becomes steady, and an exact reading can be obtained. I have given the results in Table I. in the same form as in my previous papers. The bomb used in Series 1, 2, and 4 had a capacity of 1·1764 litres at 15°; that used in Series 3, a capacity of 1·1801 litres. In Table I., the volume of the bomb will be found calculated for every temperature and pressure.

Table I.

Temperature.	Pressure.	Chlorine. Kilogrms.	Volume of the bomb in litres.	Specific gravity.
16·6	9·8—10·4	1·6703	1·1769	1·4192
26·2	7·6—9·0	1·6360	1·1772	1·3900
35·6	10—11	1·6029	1·1777	1·3610
44·2	12·5—13·5	1·5695	1·1782	1·3321
52·7	15·4—16	1·5358	1·1787	1·3029
62·5	19·2—19·6	1·4964	1·1793	1·2689
69·6	23—23·5	1·4656	1·1798	1·2262
74·0	25—26	1·4470	1·1801	1·2105
77·8	27·5—28	1·4288	1·1803	1·1943
81·7	30—30·5	1·4100	1·1806	1·1788
85·4	32—32·5	1·3919	1·1808	1·1550
90·9	36—37	1·3644	1·1813	1·1369
94·2	38—39	1·3465	1·1815	1·1140
22·7	6·5—7·4	1·6401	1·1770	1·3719
32·4	9—10	1·6156	1·1776	1·3429
41·3	11·5—12	1·5819	1·1780	1·3429
49·9	14·4—14·7	1·5477	1·1786	1·3132
58·3	17·2—17·6	1·5152	1·1790	1·2851
7·5	—	1·7078	1·1800	1·4473
21·4	6·8—7·4	1·6598	1·1807	1·4058
31·2	9·4—10	1·6256	1·1812	1·3762
40·2	11·6—12	1·5919	1·1817	1·3474
47·1	13·4—14·4	1·5664	1·1821	1·3251
55·4	16·4—17·2	1·5325	1·1826	1·2959
63·5	19·6—20	1·4994	1·1831	1·2673
66·2	22·7—23·5	1·4884	1·1833	1·2578
70·3	24—24·5	1·4686	1·1839	1·2408
76·5	26·7—27·2	1·4399	1·1839	1·2162
83·4	30·5—31·0	1·4079	1·1844	1·1887
87·2	33—33·5	1·3885	1·1847	1·1720
92·5	37—38	1·3621	1·1851	1·1493
96·2	43—44	1·3441	1·1856	1·1337
+6·6	—	1·7015	1·1762	1·4466
+0·7	—	1·7199	1·1750	1·4626
−5·2	—	1·7403	1·1757	1·4802
−10·5	—	1·7583	1·1753	1·4960
−12·0	—	1·7608	1·1752	1·4980
−16·8	—	1·7777	1·1750	1·5129
−22·0	—	1·6957	1·1748	1·5285
−30·0	—	1·8166	1·1744	1·5468
−42·0	—	1·8536	1·1739	1·5790
−44·5	—	1·8571	1·1738	1·5821
−44·8	—	1·8572	1·1738	1·5822
−45·8	—	1·8616	1·1738	1·5859

Starting from specific gravities observed directly, I have calculated the densities for every five degrees between −50° and +100°. For this purpose I took the density at 7·5° to be accurate, and corrected the other values according to the curve of the coefficient of dilatation. The mean error, calculated from the sum of the squares of the errors, is ±0·0012 for the first series, ±0·0008 for the second, 0·0009 for the third, and 0·0022 for the fourth. I have also calculated the volume at different temperatures; the volume at 0° being taken as unity. The coefficients of dilatation are applied to the volumes taken at the initial temperatures.

Table II. shows that the coefficient of dilatation of liquid chlorine increases constantly, but slowly; and that we do not observe a rapid increase at a certain temperature, as in the case of ammonia. At about 90° the coefficient of dilatation of liquid chlorine is as great as that of gases. But while carbonic anhydride and peroxide of nitrogen dilate at 0° more than their gases, this does not happen in the case of ammonia until about 65°, with chlorine at about 90°, and with sulphurous acid at about 95°.

I have also given in Table II. the results obtained by Knietsch for the purpose of showing that our results are concordant. The greatest differences are in the densities between 35° and 60°: but for these Knietsch's method, as he himself has pointed out, is less accurate.

TABLE II.

Temperature.	Density.	Volume. $V_0=1$.	Mean coefficient of dilatation.	Density according to Knietsch.
−50°	1·5950	0·9207	—	1·5945
−45	1·5829	0·9277	0·00151	1·5830
−40	1·5709	0·9348	0·00153	1·5720
−35	1·5589	0·9420	0·00155	1·5589
−30	1 5468	0·9494	0·00158	1·5485
−25	1·5342	0·9572	0·00162	1·5358
−20	1·5216	0·9651	0·00165	1·5230
−15	1·5088	0·9733	0·00169	1·5100
−10	1·4957	0·9818	0·00175	1·4965
−5	1·4823	0·9907	0·00181	1·4830
m	1·4685	1·0000	0·00187	1·4690
5	1·4545	1·0096	0·00192	1·4548
10	1·4402	1·0196	0·00199	1·4405
15	1·4257	1·0300	0·00205	1·4273
20	1·4108	1·0409	0·00212	1·4118
25	1·3955	1·0523	0·00219	1·3984
30	1·3699	1·0642	0·00226	1·3815
35	1·3640	1·0766	0·00234	1·3683
40	1·3477	1·0896	0·00242	1·3510
45	1·3311	1·1032	0·00250	—
50	1·3141	1·1175	0·00259	1·3170
55	1·2967	1·1325	0·00268	—
60	1 2789	1·1482	0·00278	1·2830
65	1·2607	1·1648	0·00289	—
70	1·2421	1·1823	0·00301	1·2430
75	1·2228	1·2009	0·00314	—
80	1·2028	1·2209	0·00333	1·2000
85	1·1821	1·2423	0·00351	—
90	1·1602	1·2657	0·00376	—
95	1·1374	1·2911	0·00402	—
100	1·1134	1·3189	0·00430	—

If we heat the bomb filled with liquid chlorine to above the temperature at which the determination of the density is made—at temperature at which it is entirely filled with liquid—the pressure increases more rapidly than at below this point when we have only to deal with the variation of the tension of the saturated vapour; this increase of pressure is by no means so great as one would imagine, for it depends on the quotient of the coefficient of dilatation divided by the coefficient of compressibility. If, therefore, we know the coefficient of dilatation of chlorine at a given temperature, we can calculate the coefficient of compressibility by observing the increase of pressure caused by a slight—though not too feeble—variation of temperature, at the same time taking into account the increase of pressure of the gaseous chlorine due to the rise of temperature. Table III. contains the observations made for this purpose and the results obtained.

In Table IV. I have given the results obtained with sulphurous anhydride, ammonia, and chlorine.

In the observations of the variations of pressure no anomalies have been noticed as in the case of sulphurous acid. But at the highest temperatures, the variations of pressure were as great as could be obtained, considering what the pressure was. We may therefore conclude that the chlorine did not attack the iron. But at the end of a series of experiments carried up to 94°, after the tap of the bomb was opened and when the temperature had been kept for some time at 15°, we noticed that it weighed 3·3 grms. more than at the commencement—and that, even when taking into account the chlorine it still contained. On washing the bomb with water, we obtained a solution of chloride of iron containing a fair amount of oxide and which deposited a greenish yellow precipitate. The metal tap was not attacked, and no copper could be found in the solution obtained. The weight of the bomb when thoroughly cleaned was 30 grms. less than its original weight. The iron had thus been attacked, and it seemed important to determine the temperature at which this reaction commences. For this purpose the bomb was filled with chlorine, and, with the tap opened, was kept at 15° in a water-bath; the tap was then closed, and, after carefully drying the apparatus, it was again weighed. This operation was repeated after bringing the bomb, filled with liquid chlorine, to 40·2°, to 63·5°, to 83·4°, and to 96·2°. The bomb, whose capacity was 1·1801 litres, weighed 3·1966 kilogrms. when empty, and 3·2004 kilogrms. when full of chlorine gas at 15°. After having been brought to 40·2° and then weighed under the conditions described above, its weight was 3·2003 kilogrms.; there was thus no variation of weight, and therefore no attack of the iron.

TABLE III.

Temperature.	Pressure observed. Atmospheres.	Variation of pressure per 1°. Atmospheres.	Calculated pressure in atmospheres	Coefficient of compressibility.
33·5°	12	—	—	—
34·0	16	—	17·3	—
34·5	21	—	22·7	—
35 0	26	—	28·0	—
35·5	31	—	33·4	—
36 0	36·5	—	38·7	—
36·5	42	—	44·1	—
37·0	47·5	—	49·4	—
37·5	53	—	54·8	—
37·9	59	—	59·1	—
37·3	52·5	10·7	52·7	0·000225
62·9	21·7	—	—	—
63·4	24·5	—	25·8	—
63·9	28·5	—	30·0	—
64·4	32·5	—	34·1	—
64·9	36·5	—	38·3	—
65·4	40·5	—	42·4	—
65·9	44·5	—	46·6	—
66·4	49·2	—	50·7	—
66·9	55·0	8·3	54·9	0·000366
89·6	37·0	—	—	—
90·0	39·5	—	39·7	—
90 5	43·0	—	43·1	—
91·0	46·5	—	46·5	—
91·5	50·2	—	49·9	—
92·0	52 5	—	53·3	—
92·5	55·5	—	56·7	—
93·0	18·0	—	60·1	—
93·3	62·0	6·8	62·1	0·000637

TABLE IV.

Sulphurous anhydride.		Ammonia.		Chlorine.	
Temp.	Coefficient of compressibility.	Temp.	Coefficient of compressibility.	Temp.	Coefficient of compressibility.
14·4°	0·000132	10·6°	0·000130	—	—
—	—	36·8	0·000183	35·4°	0·000225
66·8	0·000271	65·7	0·000317	64·9	0·000366
90·0	0·000467	—	—	91·4	0·000673

The same was the case after raising the temperature of the bomb, filled with liquid chlorine, to 83·4°; it again weighed 3·2004 kilogrms. But when the temperature had been raised to 96·2°, it weighed 3·2035 kilogrms. under the same conditions; its weight had therefore increased 3·1 grms. From these observations we may conclude that chlorine acts on iron at above 90°, and it is probable that the attack is due to the presence of a small quantity of water.

We may here remark that Knietsch, at the commencement of his research (*Liebig's Annalen*, cclix., 111), made an analogous observation. He determined the vapour-tension of liquid chlorine at a temperature above 40° in an iron U-tube; one of the branches was connected to a manometer filled with toluene or petroleum, and contained concentrated sulphuric acid, the other branch contained the liquid chlorine.

"It is apparent," says Knietsch, "that above 100° the pressures are tinged with error; for, at this temperature, under the influence of iron there is formed hydrochloric acid, by reason of the presence of hydrogen and sulphuric acid, and thus the pressure observed is a little too high. We also observe, above all when the apparatus is left to itself, and particularly at the critical point, that the pressure increases, though very slowly. If we allow a little gas to escape, the presence of hydrochloric acid can be detected therein, and we again obtain correct values for the pressures at about 100°. Thus there is also chloride of iron produced in these experiments, and this is decomposed by the sulphuric acid, forming hydrochloric acid and sulphate.

Before closing, I would say a few words concerning the transport of liquid chlorine. According to Article 50 of the German Law, Chapter B, Par. xlvi., November 15, 1892, liquid chlorine, when carried by railway, must be contained in wrought- or cast-iron or cast-steel cylinders. These cylinders must not change form, but remain intact under a pressure of 50 atmospheres; such tests must be repeated every year. These cylinders may only contain a maximum charge of 1 kilogrm. of chlorine per 0·9 litre capacity. From this it results that liquid chlorine of 1/0·9 = 1·11 density would entirely fill the cylinders; now it does not reach this low specific gravity until above 100°. The testing pressure being 50 atmospheres, and the safe limit for ordinary usage being two-thirds of this, say 33 atmospheres, we can heat the cylinders up to 90° before reaching this limit; while my previous enquiries on the transport of liquid sulphurous anhydride and ammonia show a like security for both these bodies—the cylinders may be heated to 65° if they answer the tests—the rules are still more severe for liquid chlorine.—*Zeit. f. Angew. Chem.*, July 10, 1900.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING FEBRUARY 28TH, 1901.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, March 11th, 1901.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 184 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Feb. 1st to Feb. 28th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 184 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during February has been 1·31 inches; the average fall for the last thirty-five years is 1·80 inches; this leaves a deficit of 0·49 inch, and, added to the serious deficit of last month, makes a total deficit of 1·53 inches, or 39·4 per cent on the thirty-five years' average.

Our bacteriological examinations of 481 samples have given the results recorded in the following table; we have also examined 34 other samples, from special standpipes, &c., making a total of 515 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 23 samples) ..	800
New River, filtered (mean of 118 samples) ..	5
Thames, unfiltered (mean of 23 samples) ..	5310
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 262 samples)	26
Ditto ditto .. .. highest	273
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 23 samples) ..	172
River Lea, from the East London Company's clear-water wells (mean of 32 samples) ..	18

Of the 412 samples of the impounded and filtered water supplied to London, examined bacteriologically during the past month, eighteen samples, or 4·3 per cent, were sterile. Only two samples out of the total number examined contained more than 150 microbes, and only nine samples, or 2·1 per cent of the whole number of samples examined, contained more than 100 microbes per c.c.; the mean of the excess samples being 151. Last month the excess samples amounted to 12·5 per cent of the whole number examined.

It is thus seen that the samples containing more than 100 microbes per c.c. this month are only one-sixth of the number found during the month of January, when the water supply of the metropolis was undoubtedly, as a whole, at one of its worst yearly periods.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

SOME PRINCIPLES AND METHODS OF ROCK ANALYSIS.*

By W. F. HILLEBRAND.

(Continued from p. 128).

The Sodium-Carbonate Method.

Purity of the Sodium Carbonate used as a Flux.—Notwithstanding the most earnest efforts for years, it has been impossible to procure, either in the open market or by special arrangement with manufacturers, an article of sodium carbonate which can be called chemically pure. With special precautions small lots can be prepared in the laboratory that will contain less than 1 m.grm. total impurity in 10 grms.; but such an article can not be purchased in the market, and rarely will the so-called chemically pure dry sodium carbonate contain as little as 1 m.grm. in 10 grms. The invariable contaminating substances, aside from sand and straw, which have sometimes been found in large amount, are silica, alumina, iron, lime, and magnesia, all of these going into aqueous solution with the carbonate. The chief of these impurities are usually silica, alumina, and lime. An article of the above degree of purity is satisfactory in almost all imaginable cases, since the use of the usually extravagant amount of 10 grms. for a fusion would introduce an error of but 0·1 per cent in the analysis, supposing 1 grm. of mineral to be operated on, and it would, moreover, be distributed over several constituents. This error is undoubtedly fully equalled by the introduction of dust from the air in the various long evaporations.

* *Bulletin of the United States Geological Survey*, No. 176.

Precautions in Fusing.—Special directions with regard to the fusion and its first treatment are unnecessary, except to say that ordinarily from 4 to 6 parts of flux should be used to 1 of rock, and that the flame should not be directed vertically against the bottom of the crucible, but at an angle against the side and bottom, nor should the flame be allowed to envelope the whole crucible. These precautions apply in all ignitions of reducible substances, and yet they are rarely observed. In neither case, if neglected, will there be the necessary oxidising atmosphere within the crucible; on the contrary, reduction may occur fraught with serious consequences. This is especially true if the rock contains more than traces of pyrite or other sulphide, when, after cleansing and igniting the crucible, there may appear on its interior a darkening due to oxidation of reduced iron which had alloyed with the platinum. This may in exceptional cases amount to several m.grms. in weight, and can be removed only by repeated ignitions, followed each time by scouring or treatment with hydrochloric acid or acid potassium sulphate. In order to avoid the use of nitre in case of pyritiferous rocks, it is well to first roast the weighed powder in the crucible in which the fusion is to be made.

Treatment after Fusion.—When fusion is complete, the crucible is seized with the tongs (Fig. 1, p. 69), and the contents are caused to solidify in a thin sheet over the sides and bottom by imparting an appropriate rotating motion with the arm during the cooling process. This is far preferable to allowing the melt to form a thick cake at the bottom, since much less time is required for disintegration, and separation from the crucible is usually much easier.

It sometimes happens that the cooled flux, and even its solution, will indicate absence of manganese when it is really present in quantity to give normally a strong colouration. Two fusions made side by side or successively, under apparently similar conditions, may in one case show little or no manganese, in the other considerable. This observation has been frequently made, and therefore the absence of a bluish-green colour in the fusion is not to be taken as proof of the absence of manganese. This difference of behaviour I can ascribe to no other cause than that of a reducing atmosphere in one of the crucibles, and an oxidising one in the other, even though the conditions were apparently alike.

The contents of the crucible are placed in a rather tall covered beaker with some water, and hydrochloric acid of 1·1 specific gravity is added in excess. The depth of the pink colour usually produced on addition of the acid allows of judging approximately as to the amount of manganese present. The beaker is placed on the water-bath, and when disintegration is complete, having been assisted by gentle pressure with a blunt glass rod, the contents are transferred to a large platinum dish and evaporated on the bath.

Subsequent Treatment.

From this point the treatment will ordinarily be the same whether the boric-oxide or the sodium-carbonate method of decomposition has been employed.

Drying and Testing of Silica.—As to the best way of rendering silica insoluble by evaporation, the writer's predilection is for a double evaporation instead of a single one on the water-bath. By fusing with sodium carbonate in the forenoon, the silica is ready for the first filtration in the afternoon. It is quite unnecessary to carry the evaporation beyond approximate dryness. The filtrate is again evaporated, always in platinum, and is ready for final filtration the following morning, when approximately 1 per cent of silica is recovered and added to the main portion. The writer's experience is that a better separation of silica is effected hereby, and in no more time than by a single long evaporation. That which is subsequently recovered from the precipitate of alumina, &c. (see *prox.*, "Recovery of Silica," &c.), rarely exceeds a half or, at the most, 1 m.grm.

Drying in an air-bath at 110° C. or higher, or on a hot plate or sand-bath, or even over a free flame, in order to render silica insoluble, offers no advantage unless much magnesium is present, and then the most favourable temperature, according to Gilbert (*Technology Quarterly*, 1890, vol. iii., p. 61; Abstract in Fresenius's *Zeit. fur Anal. Chemie.*, 1890, vol. xxix., p. 688), is 120° C. The presence of much calcium chloride seems to facilitate dehydration of the silica, while magnesium chloride above 120° C., on the other hand, by decomposing, forms a silicate which dissolves in hydrochloric acid, and increases the amount of silica carried into the filtrate. It does not appear from Gilbert's paper that the blast-furnace slags, on which he experimented, contained titanium, phosphorus, or iron in appreciable amounts. Basic magnesian rocks usually do, and in such cases it is probable that the employment of a drying temperature of 120° would materially add to the large impurity always to be expected with the silica. In other cases he confirms the earlier belief that drying temperatures higher than that of the water-bath increase the amount of insoluble impurity, chiefly alumina, in the silica, and that this amount can not be reduced by long digestion with hydrochloric acid. Further, he confirms Lindo's statement that evaporation with sulphuric acid till the appearance of white fumes gives a higher result in silica than with hydrochloric acid. But for general rock analysis the use of sulphuric acid at this stage must be rejected utterly.

Blasting for twenty to thirty minutes* is necessary to expel all moisture from the silica, and it is then not hygroscopic. Its weight should always be corrected for impurities, which are never absent, by evaporating with hydrofluoric and sulphuric acids, and again blasting. If toward the end of evaporation with these acids, when the hydrofluoric acid has been driven off and the sulphates begin to appear in solid form, the residue has a peculiar milky or enamel-like appearance, it may be taken as evidence of much phosphorus and titanium. This appearance is possibly due to zirconium with the phosphorus and titanium (see footnote, *prox.*), and is so unusual and striking that it is worth while calling attention to it. With basic rocks very rich in titanium and phosphorus the residue may amount to 2 or even 3 per cent of the rock.

The subsequente precipitate of alumina, &c., is usually ignited in the crucible containing the residue from the silica.

It might be supposed that this residue would contain most of the barium of those rocks carrying that element, together with sulphur or sulphates, but the reverse is true as a rule. Only when there is a considerable excess of SO_3 over the BaO will much of the latter be found there, and in the vast majority of cases there is none at all. Should some be present, its removal and estimation at this stage is not necessary, as it can be more conveniently recovered later, together with the silica accompanying the alumina, &c., precipitate (see *prox.*).

The separation of silica in rocks containing fluorine has been touched upon in commenting on the boric-oxide and sodium-carbonate methods of fusion (see p. 127, and footnote, p. 128), and will be considered further under the head of "Fluorine."

Platinum in Filtrates.—The filtrates from the silica always contain notable amounts of platinum. This arises in very small degree from the crucible fusion, in a larger one indirectly from the action of hydrochloric acid on manganate, vanadate, and sometimes chromate of sodium, and, if much iron is present, in no small degree from the reduction of ferric chloride to ferrous by the platinum of the dish. This last reaction is little known, apparently,

* It must be borne well in mind that some platinum crucibles lose weight steadily and very appreciably on long blasting, not only when new, but even after long use. When a crucible suffers from this defect the rate of loss should be ascertained from time to time, and allowance made accordingly, or else the weight of the crucible should be taken after and not before ignition of the precipitate. (See on this subject Hall, *Journ. Amer. Chem. Soc.*, 1900, vol. xxii., p. 494).

but is mentioned in Gmelin-Kraut (*Anorg. Chem.*, vol. iii., p. 359, Sixth revised edition), and can be readily demonstrated by evaporation of ferric chloride in platinum.

The removal of this platinum before precipitating alumina and iron is not necessary (but see footnote, *prox.*), and to do so involves the re-oxidation of all iron and subsequent boiling to remove or destroy the excess of oxidising agent, together with the expenditure of much valuable time. The iron is already oxidised by the fusion, and needs no further help in that direction. Nevertheless, if time is not a prime object, its removal by hydrogen sulphide is to be recommended. In the following descriptions, however, it is assumed that the platinum has not been gotten rid of at this stage.

VII.—*Metals Precipitable by Hydrogen Sulphide.*

The preaence in appreciable amounts of metals precipitable by hydrogen sulphide, except perhaps copper, is of such infrequent occurrence in most rocks that discussion is unnecessary in their connection. In case it is necessary to precipitate them at this stage, however, it is always well to bear in mind that a little titanium may be thrown down along with them. Separations of the silica should be made in porcelain, to eliminate platinum, or, better still, the quantitative estimation of these metals should be made in a separate portion of the rock broken up by the action of hydrofluoric and sulphuric acids.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 7th, 1901.

Dr. PERKIN, F.R.S., Vice-President, in the Chair.

MESSRS. T. H. Page and James Moir were formally admitted Fellows of the Society.

The following certificates were read for the first time:—Ernest Clarke, 9, Polygon Avenue, Stockport Road, Manchester; Thomas Kennedy Cockburn, 26, Elm Street, Whiteinch, Glasgow; Eustace Coddington, 131, St. James' Road, Upper Tooting, London, S.W.; Hugh Edward Ellis, 18, Belmont Road, Aberdeen; John Vargas Eyre, 26, Bridge Road West, Battersea Park, S.W.; Francis Robert Henley, Watford, Rugby; Charles Edward Kenneth Mees, 33, St. Saviour's Road, Croydon; Arthur Peacock, Smithies Bridge House, Heckmondwike, Yorks.; William Hammond Robinson, The Limes, Painswick Road, Cheltenham; Henry Ewing Smith, 22, City Road, London, E.C.; William Henry Taylor, 19, Shafton Road, Victoria Park Road, N.E.

Of the following papers, those marked * were read:—

*29 "*Nomenclature of the Acid Esters of Unsymmetrical Dicarboxylic Acids.*" By J. J. SUDBOROUGH.

After mentioning the systems adopted by Brühl, Wegscheider, and Anschütz, the author suggested the following nomenclature.

Of the two isomeric monoalkyl esters of an unsymmetrical dibasic acid, that ester be termed the α-compound which has the higher esterification constant, and the other with the lower constant the β-compound.

The advantages of this system are:—(1). Similarly constituted esters receive similar names; (2) in the case of many of the simpler acids, the substituent which produces the want of symmetry is in the α-position to the alkylated carboxylic group; (3) ease with which the two esters may be identified.

*30. "*Additive Compounds of α- and β-naphthylamine with Trinitrobenzene Derivatives.*" By J. J. SUDBOROUGH.

The red needles which were obtained when α-naphthylamine trinitrobenzoate was boiled with alcohol (*Trans.*, 1899, lxxv., 588), are an additive compound of trinitrobenzene with α-naphthylamine. A number of other similar compounds have been obtained; all are red or reddish-purple in colour, are remarkably stable, may be crystallised from glacial acetic acid, and are only slowly decomposed by cold dilute hydrochloric acid; they are also stable when exposed to the air, and in these properties differ from the additive compounds of trinitrobenzene, with aniline, toluidine, &c., described by Hepp (*Annalen*, 1882, ccxv., 344).

The following are the compounds which have been prepared:—*α-Naphthylamine trinitrobenzene*, m. p. 214°; *β naphthylamine trinitrobenzene*, m. p. 162°; *α-naphthylamine trinitrotoluene*, m. p. 141·5°, the *β-isomeride*, m. p. 113·5°; *α-naphthylamine picramide*, m. p. 203°, and the *β-isomeride*, m. p. 161·5°; *α-naphthylamine ethyltrinitrobenzoate*, m. p. 135°, and the *β-isomeride*, m. p. 126°; *α-naphthylamine ethylpicrate*, m. p. 79·5°; and *α-naphthylamine methylpicrate*, m. p. 75°.

With the object of determining the constitution of these compounds, the action of acetic anhydride and of alcoholic potash on them has been studied; it was thought probable that these reagents might indicate the presence of a hydroxyl group.

α-Naphthylamine trinitrobenzene and acetic anhydride warmed for a few minutes yield a monoacetyl derivative, which crystallises from benzene in sulphur-yellow needles melting at 140·5°. The compound has the acetyl group attached to nitrogen, as the same substance may be obtained by the direct union of trinitrobenzene and α-acetnaphthalide, and as it yields α-acetnaphthalide on treatment with methyl alcoholic potash. Several similar acetyl derivatives have been prepared.

A methyl alcoholic solution of potassium hydroxide decomposes the red compounds, yielding the potassium derivative of trinitrobenzene described by Lobry de Bruyn.

*31 "*Acetylation of Arylamines.*" By J. J. SUDBOROUGH

According to Ulffers and von Janson (*Ber.*, 1894, xxvii., 93), acid ortho-substituents retard the introduction of an acetyl group into a primary arylamine, but at the same time facilitate the introduction of a second acetyl group. Quantitative experiments have been made by boiling aniline, *o*-toluidine, *p*-toluidine, pseudocumidine, α- and β-naphthylamines with acetic anhydride for an hour, and determining the percentage of the arylamine converted into mono- or di-acetyl compounds. The results indicate that a methyl or phenylene group in an ortho-position facilitates diacetylation. All *o*-substituents, whether of a positive or negative character, thus appear to have the property of accelerating the formation of diacetyl derivatives of primary arylamines.

The following new compounds were described: *Diacetylpseudocumidine*, $C_6H_2Me_3{\cdot}NAc_2[Me_3:N=1:2:4:5]$, well developed, transparent prisms melting at 69·5°; *diacetyl-α-naphthylamine*, $C_{10}H_7NAc_2$, colourless, hard prisms melting at 130°; *diacetyl-β-naphthylamine*, colourless plates melting at 66·5°; and *diacetyl-2:6-dibromaniline*, large prisms melting at 100°. Most of these diacetyl derivatives crystallise remarkably well, and are readily soluble in the ordinary organic solvents.

*32 "*Formation of Amides from Aldehydes.*" By R. H. PICKARD and W. CARTER.

When an aldehyde is oxidised with ammonium persulphate in the presence of lime, a 30—40 per cent yield of the amide of the corresponding acid is obtained. The greater portion of the remainder of the aldehyde can be recovered unchanged, and by further oxidation the yield of amide can be increased to 70 per cent of the weight of aldehyde taken. Substituted amides can be obtained by using potassium persulphate and an amine.

*33. "*A Method of Isolating Maltose when Mixed with Glucose.*" By A. C. HILL, M.A.

This method is, essentially, one of removal of the glucose by fermentation with *Saccharomyces Marxianus*, a yeast observed by Hansen in 1888 as not fermenting

maltose. It includes also certain details of procedure, which have been found to facilitate, even if they are not necessary to, an easy crystallisation of the maltose after the fermentation is over, and reduce to a minimum such adventitious impurities as the by-products of fermentation and the oxidation products of the sugars.

A pure culture of the yeast, which has been grown in a glucose broth, is washed repeatedly with sterilised tap water, making use of a centrifuge, and is then added to a sterilised solution of the sugars which it is desired to ferment. The solution, which may be in an ordinary flask closed by a cotton-wool plug, should not contain much more than 10 per cent of sugar, and should be made up in part with sterilised tap water.

The fermentation is conducted at 25—29°, and proceeds slowly in the absence of proteid, and without any notable multiplication of the yeast cells. When the evolution of carbon dioxide has nearly ceased, the flask is heated for a minute or so at 100° in the autoclave, and then its contents are freed from cells by filtration through a porous funnel. Alcohol is added to the solution to one-third of its volume, and the whole evaporated down in a current of carbon dioxide to a thick syrup under diminished pressure; if necessary, more alcohol is added during the evaporation, so that the temperature does not rise above 60°. The rest of the process resembles that usually employed in the re-crystallisation of maltose from 80 to 85 per cent ethyl alcohol, and results in the separation of the maltose quite white at the first crystallisation.

34. "*The Vapour Pressure of Aqueous Ammonia Solution.*" By E. P. Perman, D.Sc.

The vapour pressure of aqueous ammonia solutions of concentrations varying from nothing to 35 per cent has been found by a statical method; the temperatures ranged from 0° to 60°. The curves showing the variation of pressure with concentration at various temperatures are found to be approximately represented by the equation $p(100-c)=ac+bc^2$; a and b are constants, c is the concentration of the ammonia in the solution.

The equation may be put in the form $p(100-c)=c.k$, when $k=a+bc$, and is the reciprocal of the solubility coefficient. The variation of pressure with temperature (the concentration remaining constant) is expressed with fair accuracy by the equation $\log.p=\alpha+\beta t+\gamma t^2$, α, β, and γ being constants, of which γ is always negative.

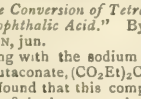
The constant β is found to have the same value as the corresponding constant found in the expression $\log.b=\alpha'+\beta' t$ for the *rate of escape* of ammonia from aqueous solution (*Trans.*, 1898, lxxiii., 511).

35. "*The Influence of Sodium Sulphate on the Vapour Pressure of Aqueous Ammonia Solution.*" By E. P. Perman, D.Sc.

The author has determined the vapour pressures of ammonia solutions containing sodium sulphate in solution at temperatures varying from 26° to 47°, and has compared them with corresponding solutions of ammonia without sodium sulphate. The curves show no break at 33°, nor do they diverge more than those for ammonia solution. Hence it seems probable that the sodium sulphate does not exist as a hydrate in solution.

36. "*Formation of Aromatic Compounds from Ethyl Glutaconate and its Derivatives. The Reduction of Trimesic Acid and the Conversion of Tetrahydrotrimesic Acid into Tetrahydroisophthalic Acid.*" By W. T. Lawrence and W. H. Perkin, jun.

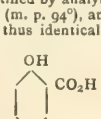
In experimenting with the sodium compound of ethyl sodio-dicarboxyglutaconate, $(CO_2Et)_2CNa{\cdot}CH{:}C(CO_2Et)_2$, the authors have found that this compound, when heated with alcohol at 150°, is decomposed with formation of a large yield of *ethyl trimesate*,—



and further, that methyl sodiodicarboxyglutaconate under the same conditions is converted into *methyl trimesate*.

When the sodium compound of ethyl glutaconate, $CO_2Et{\cdot}CHNa{\cdot}CH{:}CH{\cdot}CO_2Et$, is heated with alcohol at 150°, it is also decomposed, but in a different manner, and the product on hydrolysis yields *hydroxyisophthalic acid*.

This acid was identified by analysis, and by conversion into the methyl ester (m. p. 94°), and into the ethyl ester (m. p. 52°), and it is thus identical with the hydroxyisophthalic acid,—



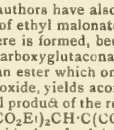
which Kupferberg (*Journ. Prakt. Chem.*, 1877, [2], xvi., 428), obtained by heating sodium salicylate in a current of carbon dioxide.

When ethyl methylglutaconate,—

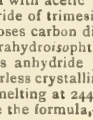
$$CO_2Et{\cdot}CHMe{\cdot}CH{:}CH{\cdot}CO_2Et,$$

is heated with sodium ethylate and alcohol at 140°, it yields a solid ester melting at 96° which, on hydrolysis, is converted into an acid very sparingly soluble in water, and melting at 216°; these substances are at present under investigation. The authors have also found that when the sodium compound of ethyl malonate is digested with ethyl trichloroacetate there is formed, besides the sodium compound of ethyl dicarboxyglutaconate (Ruhemann, *Ber.*, 1896, xxix., 1017), an ester which on hydrolysis and elimination of carbon dioxide, yields aconitic acid. This ester, which is the normal product of the reaction, therefore must have the formula $(CO_2Et)_2CH{\cdot}C(CO_2Et){:}C(CO_2Et)_2$.

When trimesic acid, dissolved in sodium carbonate, is treated with sodium amalgam, it is readily reduced with formation of a mixture of acids, which are evidently stereoisomeric modifications of tetrahydrotrimesic acid,—



One of these acids has been isolated in a pure condition; it melts at about 210°, and is very sparingly soluble in dry ether. When digested with acetic anhydride it yields a resinous double anhydride of trimesic acid and acetic acid, which on distillation loses carbon dioxide, with formation of the anhydride of tetrahydroisophthalic acid. On treatment with potash this anhydride yields tetrahydroisophthalic acid as a colourless crystalline substance sparingly soluble in water, and melting at 244°; from its method of formation it must have the formula,—



and is the first tetrahydroisophthalic acid which has so far been prepared. The authors are continuing their investigation on the action of sodium ethylate on the derivatives of glutaconic acid, and other similarly constituted acids.

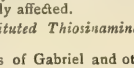
37. "*Optical Activity of certain Ethers and Esters.*" By P. A. Guye.

The author has confirmed the results of Tschugaeff's observations, quoted by McCrae and Patterson (*Trans.*, 1900, lxxvii., 1096), that the optical rotation of compounds containing the phenacetyl group resembles more closely that of compounds containing the acetyl or the chloroacetyl group, than that of compounds containing the toluyl group, although the mass of the phenacetyl group is more nearly that of the toluyl group than of either of the other groups named. The examination of a number of compounds of amyl (phenyl-amyl oxide, benzyl-amyl oxide,

and various amyl esters) has led the author to an analogous conclusion. It is, however, only one case of a more general conclusion already drawn by him, namely, that when substitutions of chains or groups of elements are effected in an asymmetric carbon compound, sufficiently far from the asymmetric carbon atom, the optical rotation is only slightly affected.

38. "*Halogen-substituted Thiosinamines.*" By A. E. DIXON, M.D.

From the researches of Gabriel and others, as well as from his own previous work, the author thought it not unlikely that the "chlorallylthiourea" of Henry (*Ber.*, v., 188), obtained from β-chloroallylthiocarbimide and ammonia, might really be the hydrochloride of a ring-compound,—

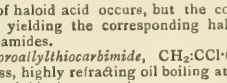


to test this, he has prepared the thiocarbimide, and examined a number of its compounds with bases.

Contrary to anticipation, the addition products so obtained are not closed chain saline derivatives; no formation of haloid acid occurs, but the constituents unite directly, yielding the corresponding halogen-substituted thiocarbamides.

β-Chloroallylthiocarbimide, $CH_2{:}CCl{\cdot}CH_2{\cdot}NCS$, is a colourless, highly refracting oil boiling at about 182°; it is slightly soluble in water, has a very pungent odour, and readily blisters the skin.

With ammonia it yields Henry's β-chloroallylthiourea; prisms, melting at 93·5—94·5° (corr.); Henry gives 90—91°. This substance is moderately soluble in water, and easily so in alcohol; the latter solution, if moderately dilute, gives no precipitate with silver nitrate, but is freely desulphurised by warming with alkaline lead tartrate. Chloroallylthiourea undergoes no isomeric change if boiled in aqueous solution; when fused with monochloracetic acid, it yields the hydrochloride of *β-chloroallylthiohydantoin*,—



white prisms, which begin to decompose at about 170°, and lose the combined acid on re-crystallisation from water. The free thiobydantoin is deposited from water in leaves, and from alcohol in prisms, both forms melting at 149°; when hydrolysed by boiling with dilute alkali, thioglycollic acid is produced.

ab-*Chloroallylphenylthiocarbamide*,—

$$CH_2{:}CCl{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_5,$$

prepared from the thiocarbimide and aniline, is deposited from benzene in plates, m. p. 91—92°. When desulphurised by silver nitrate it gives rise to the corresponding ab-*chloroallylphenylcarbamide*, as slender prisms, m. p. 151—152°.

ab-*Chloroallylorthotolylthiocarbamide* separates from weak alcohol in prisms, m. p. 84—85°.

ab-*Chloroallylbenzylthiocarbamide* crystallises from a mixture of benzene and light petroleum in very brilliant prisms, m. p. 69°. Unlike the preceding thiocarbamides, it is not desulphurised when boiled with alkaline lead tartrate.

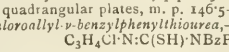
Piperdine yields *chloroallylpiperidylthiourea* in transparent quadrangular plates, m. p. 146·5—147·5°.

n-*Chloroallyl-ν-benzylphenylthiourea*,—

$$C_3H_4Cl{\cdot}N{:}C(SH){\cdot}NBzPh,$$

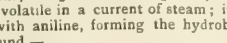
is deposited from light petroleum in needles, m. p. 77—78°.

β-Chloroallylthiocarbimide, dissolved in chloroform, absorbs bromine, yielding *β-chloro-βγ-dibromopropylthiocarbimide*, $CH_2Br{\cdot}CClBr{\cdot}CH_2{\cdot}NCS$, a dense, yellowish liquid, volatile in a current of steam; it unites spontaneously with aniline, forming the hydrobromide of a ring compound,—



The hydrobromide occurred as a sandy powder, m. p. 112—113°; when treated with cold alkali, hydrogen bromide was removed, but the base could not be obtained in a state fit for analysis.

With benzylamine an oily hydrobromide was produced; from this potash withdraws a molecule of hydrogen bromide, leaving the free base,—



which crystallises in prisms, m. p. 107—108°, and dissolves in hydrobromic acid to re-form the oily hydrobromide.

39. "*A Form of Tautomerism Occurring amongst the Thiocyanates of Electro-negative Radicles.*" By A. E. DIXON, M.D.

Some years ago (*Trans.*, 1897, lxxi., 640; see also 1899, lxxv., 389), the author remarked that the so-called "phosphorus trithiocyanate," $P(SCN)_3$, appeared to possess thiocarbimidic as well as thiocyanic properties, and subsequent investigation tends to show that this power to function in both capacities is also manifested by the products obtainable from metallic thiocyanates and the chlorides of a number of electro-negative mineral elements and compound-radicles.

The chlorides, dissolved in suitable anhydrous solvents, were caused to interact with excess of lead or other metallic thiocyanate, if possible, until the chlorine was completely eliminated as metallic chloride; the solid residue was then filtered off, and the filtrate treated with a base such as aniline. Precipitates were thus obtained, which gave the desulphurisation tests with lead and silver salts, characteristic of thiocarbamides, and were usually hydrolysed by contact with water so as to afford the substituted thiourea corresponding to the base used. Unfortunately, no efficient method has yet been found for purifying these precipitates, which are rarely free from more or less contamination with basic thiocyanate.

"Phosphorus trithiocyanate," $P(SCN)_3$, gave with aniline a yellow solid insoluble in cold water, but decomposed when boiled with water into phenylthiourea and an acid of phosphorus; this substance is probably phosphorus triphenyltrithiourea, $P(NH{\cdot}CS{\cdot}NH{\cdot}C_6H_5)_3$. With *o*-toluidine a yellow powder, melting between 81° and 83° was obtained; it appears to be the corresponding tolyl derivative nearly pure. Both these compounds are very freely soluble in alcohol and acetone, but nearly insoluble in benzene, chloroform, and light petroleum.

"Phosphoryl trithiocyanate," $PO(SCN)_3$, obtained in solution by boiling phosphorus oxychloride in dry cumene with lead thiocyanate, gave with silver and lead salts the usual thiocarbimidic reactions, and united spontaneously with aniline, *o*-toluidine, and dry ammonia.

The *aniline* compound was a pale yellow powder melting at about 111—112°, freely soluble in alcohol, ethyl acetate, acetone, glacial acetic acid, and nitrobenzene; insoluble, or nearly so, in chloroform, ether, carbon disulphide, benzene, and light petroleum. It was nearly insoluble in cold water, but dissolved gradually on boiling; the solution contained phosphoric and thiocyanic acids, and on cooling, gave a crystalline deposit of phenylthiourea. The latter appears to be formed by hydrolysis of phosphoryltriphenyltrithiocarbamide:—

$$PO(NH{\cdot}CS{\cdot}NH{\cdot}C_6H_5)_3+3H_2O=H_3PO_4+3CSN_2H_3{\cdot}C_6H_5.$$

Orthotoluidine gave a tenacious oil, hardening presently to a resin-like solid; its properties resembled those of the phenylic homologue, but the substance could not be obtained in a pure condition.

Dry *ammonia* gas yielded a pale yellow granular solid, melting, imperfectly, below 60°, readily soluble in water, and containing a very appreciable quantity of ammonium thiocyanate. The solution in cold water gave with excess of ammonia, followed by magnesia mixture, scarcely any precipitate. But this solution, if previously boiled and allowed to cool, then reacted freely with the above test;

consequently, it is inferred that the phosphoric acid does not exist ready formed in the solution, but originates through the hydrolysis of the phosphoryltrithiourea, $PO(CSN_2H_3)_3$.

The "thionyl thiocyanate" of McMurtry (*Trans.*, 1889, lv., 48), differs in physical and chemical characters from all the known electro-negative thiocyanates; it is suggested that this compound, of which the thiocyanic properties are very feebly marked, whilst it gives decided thiocarbimidic reactions, is probably a polymeric form, $[SO(NCS)_2]_n$.

Carbonyl chloride, in toluene, reacted with lead thiocyanate on standing; the dissolved sulphuretted product (which was freely desulphurised by lead and silver salts) combined at once with aniline, yielding in small quantity a substance melting at about 174° and possessing the characters of a thiocarbamide.

Annual General Meeting.

The Annual General Meeting of the Society for the Election of Officers and other business will be held on Thursday, March 28th, at three o'clock in the afternoon.

CORRESPONDENCE.

AMERICAN SPELLING OF CHEMICAL WORDS.

To the Editor of the Chemical News.

Sir,—In your issue of February 8th, 1901 (vol. lxxxiii., p. 71), the reviewer of a book published in the United States speaks favourably of it, but says:—"It is a pity that this useful manual has not been translated into English," and he objects to the spelling of certain words, "sulfur," "oxid," &c. Similar criticisms on American books have appeared in the Chemical News at intervals during recent years, and readers of these reviews might infer that the unfamiliar spelling was merely an idiosyncracy of the author. Such criticisms, however, show that the reviewers fail to recognise that the American authors use a definite system, endorsed by high authorities in the United States, and have not devised novel forms simply to be thought eccentric.

At the meeting of the American Association for the Advancement of Science, held at Cleveland, Ohio, in 1888, the Chemical Section appointed a Committee consisting of Professors T. H. Norton, Edward Hart, H. Carrington Bolton, and Jas. Lewis Howe, to secure by correspondence and by personal contact the consensus of opinion held by American chemists on the "Spelling and Pronunciation of Chemical Terms." This Committee formulated a body of rules, and during three succeeding years they were discussed in extended correspondence, and orally at the intervening meetings of the Chemical Section held at Toronto and at Indianapolis; finally, at the Washington meeting, held in 1891, the report was formally adopted. Almost immediately thereafter, the United States Bureau of Education gave its sanction to the reformed spelling, and greatly promoted its use by printing the Rules in chart form, and sending thousands of copies to educational institutions throughout the country. Since then the improved method has gradually come into vogue; many writers of text-books use it, one widely circulated English dictionary has adopted it, and many chemists prepare their manuscripts with the reformed spelling, though some editors change the style before printing the communications. The new system has the merit of simplicity, lucidity, and uniformity, and it is founded on a logical basis, so it is rapidly becoming the standard system in the United States.

I do not propose to enter upon details at this time, but I wish to point out that the word "sulphur," spelled as if derived from Greek, is etymologically incorrect, and being replaced by "sulfur" on this side of the Atlantic. Those seeking full details will find the rules for spelling in the *Proceedings of the American Association for the Advancement of Science*, vol. xl.; *Journ. Analyt. Applied Chem.*, March, 1892, vol. vi.; Witthaus' "Medical Students' Manual of Chemistry"; and in the *Annual Report U.S. Bureau of Education*, 1893-94, pages 873-876.

The disfavour with which such reform is received in Great Britain has its counterpart in the United States, where objection is made to the ultra conservatism that causes British writers to retain the old-fashioned and erroneous forms, and thus hamper progress in the right direction. Americans in reviewing books from across the Atlantic do not make unfavourable comments every time that they notice archaic spellings; pray "let us have peace," and a discontinuance of even gentle reminders of the error of our ways (?) in the matter under discussion, for the reformed spelling has come to stay, and criticisms of those we honour and esteem in the mother country will not dissuade our writers from the upward movement.

Allow me to add that I am not acquainted with the American author whose book has been reviewed, and this letter has been written not in defence of his action but rather in hopes of enlightening others.—I am, &c.,

H. Carrington Bolton.

Washington, D.C.

PROUT'S HYPOTHESIS AND RADIO-ACTIVE ELEMENTS.

To the Editor of the Chemical News.

Sir,—Many chemists believe that the fact that most of the seventy odd elements have atomic weights differing by only a small amount from whole numbers is something more than a mere accident. The recent discovery of a number of heavy radio-active elements raises the question how far the presence of minute quantities of unknown elements may have affected the accuracy of atomic weight determinations.—I am, &c.,

Geoffrey Martin.

Bristol, March 13, 1901.

ANALYSIS OF HEN-DUNG.

To the Editor of the Chemical News.

Sir,—In January last I collected a clean fresh sample of hen-dung, which, after removing pebbles (grit supplied to the fowls), I found to contain:—

Water	64·25
*Organic matter	24·28
Alumina	0·42
Ferric oxide	0·54
Lime	1·72
Magnesia	0·40
Phosphoric anhydride	0·79
Sulphuric anhydride	0·70
Chlorine	0·05
Sand and insoluble matter	5·79
Potash	0·36
Soda	0·03
	99·33

* Containing—Ammonia, 0·77 p.c.; Total Nitrogen, 1·05 p.c.

Of course different food must cause considerable variations, but the above numbers for the three chief manurial ingredients are strikingly lower than the average values quoted by Storer (N 1·60, P_2O_5 1·7, K_2O 0·8) and Ulrich (N 1·2—2·4, P_2O_5 3·0—4·2, Alkalis 2·0—2·2), especially the phosphoric acid and potash. It would appear, therefore, that fowl-dung may sometimes be by no means a highly concentrated manure. The above percentage of

K_2O is less than Wolff's average (0·5) for farmyard manure.

It will be noticed that there is a considerable percentage of sulphur; as the fowls were doing very little laying possibly this might be larger than usual, as less would be required for the formation of albumen. The manurial ingredients, however, might also be expected to be larger on this account; but as the birds had not completely recovered from moulting a special drain might result. Can anyone inform me if large variations occur in different seasons with birds fed throughout with similar food?—I am, &c.,

L. V. Wright.

Pocklington, March 16, 1901.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxii., No. 8, February 25, 1901.

Certain Conditions of Reversibility.—Albert Colson.—The author performed various experiments on the dissociation of silver carbonate in order to find whether carbonic oxide behaves in the same way as hydrogen with regard to silver oxide. Towards 10°, the reduction of the metallic oxide by CO is extremely rapid, white silver being deposited. At −21° the reduction is very slight; however, the gaseous CO is totally absorbed, but in most cases it is in a great measure replaced by a corresponding quantity of carbonic anhydride.

Compressibility of Solutions.—M. Guinchant.—The author investigates the relation between the volume of a dissolved substance and the pressure. His experiments show that the volume of the dissolved body is independent of the pressure; at least, up to the pressure of four atmospheres. It is therefore probable that the variation in volume which accompanies the simple solution of a body in water is due to a variation in the state of aggregation of the solvent rather than to the volume occupied by the dissolved molecules. By this last hypothesis, the variation in volume, independent of the pressure, must be regarded as representing the co-volume of the dissolved body.

Indium.—C. Chabrié and E. Rengade.—The authors' researches were made on the alums of indium and the alkaline metals, cæsium, and rubidium. These were decomposed by heat into oxide of indium, barium sulphate, and cæsium or rubidium sulphate, all three substances being accurately estimated. The numbers obtained agree very well with the formula $SO_4Rb_2+(SO_4)_3In_2+24H_2O$. Indium acetylacetonate is not volatile without decomposition, and so, to determine the atomicity of indium, the rise in boiling-point of a solution of indium acetylacetonate in ethylene bromide has to be determined; this gives a molecular weight of 405, and is a further proof that indium is trivalent.

A New Crystalline Sulphate of Molybdenum.—M. Bailhache.—Sulphuric acid dissolves molybdic acid when heated, and forms with it a molybdic sulphate, MoO_3SO_3, which has been known for some time. This compound consists of colourless crystals, which are very soluble in water and are deliquescent. If the sulphuric solution is now reduced, it becomes blue, but no further crystalline body can be obtained. However, under certain conditions, it is possible to obtain with great facility a new compound derived by the reduction of the double anhydride MoO_3SO_3, and perfectly crystalline. A rapid current of hydrogen sulphide is used for the reduction. The substance is produced in the form of a crystalline sand, very dark olive-green in colour, and analysis shows it to have the formula $Mo_2O_5.2SO_3$.

New Reactions of Organo-metallic Derivatives. α-Alcoyl-β-ketonic Ethers.—E. E. Blaise.—In a previous paper, the author showed that organo-metallic derivatives react on bodies containing the nitrile function, giving compounds which, when decomposed by water, give rise to ketone derivatives. The present paper contains an account of the α-alcoyl-β-ketonic ethers which can be obtained by this method. These ethers are produced when nitriles are condensed with α-bromated ethers of the homologous acids of acetic acid in presence of zinc.

Action of Organo-metallic Derivatives on Ether Salts.—A. Béhal.—The alcoylo-halogen derivatives of magnesium react on the ether-salts of the cyclic series, and their action can be considered as taking place in three phases. In the first, a molecule of the organo-metallic derivative is fixed on to the ether salt; in the second, a second molecule of the organo-metallic derivative is fixed, and a molecule of magnesium iodoalcoylate is eliminated; finally, in the last phase, a carbide of the ethylenic function is formed.

Synthesis of Tertiary Alcohols of the Fatty Series.—Henri Masson.—The author examined the action of the organo-metallic derivatives on the derived ethers of the monobasic acids of the fatty series. At first he used organo-metallic derivatives of zinc, but finally utilised the organo-metallic derivatives of magnesium, which are more tractable than those of zinc, and with which the reactions are sharper. In all cases he obtained the tertiary alcohols.

Absorption-spectra of the Indophenols, and Colouring-matters of Triphenylmethane.—C. Camichel and P. Bayrac.—The authors conclude from their experiments that the law of auxochromes no more exists for the compounds of triphenylmethane than for the indophenols. The replacing of a tertiary nitrogen by a primary nitrogen, and the number of tertiary nitrogens, are the factors having a great influence on the absorption of light; but the law applying to this phenomenon has yet to be found. The authors have examined the influence of concentration on the alcoholic solutions of the indophenols, and on the aqueous solutions of the colouring-matters of triphenylmethane, but up to now they have always found that the coefficient of absorption is proportional to the concentration.

Constitution of Glucose.—L. J. Simon.—The aldehydic properties of glucose are represented by the linear formula of Berthelot, Fittig, and Kiliani, $CH_2OH-CHOH-CHOH-CHOH-CHOH-CHO$. This formula agrees with the processes of reduction and oxidation, with the fixation of hydrocyanic acid realised by Kiliani, and it agrees well with the stereo-chemical researches of Fischer, but it leaves unexplained certain interesting points which are discussed by the author in this paper.

Journal de Pharmacie et de Chimie, Series 6, Vol. xii., No. 7.

Estimation of Glycerophosphate of Quinine.—M. Prunier.—Two grms. of the glycerophosphate are dissolved by means of 10 or 15 c.c. of $\frac{1}{10}$th N nitric acid, and precipitated by a sodic solution containing about 6 grms. of alkali. Filter, and wash the quinine on the filter, dry at 110°, and weigh. The total filtrate, carefully measured, is divided into two equal parts. The first, used for the estimation of the acid, is supersaturated with nitric acid after the addition of 2 or 3 grms. of saltpetre, then evaporated to dryness under a funnel. Then proceed as above, by repeated additions of nitric acid, to obtain first a white ash, and then the melted mass which contains the whole of the phosphoric acid. The other half of the solution serves to complete the estimation of the quinine. For this purpose more alkali is added; then boil so long as a white pearly material separates out; this is collected on a filter. The filtrate is again boiled, and when no more

than a slight cloudiness is formed, shake up with about 50 c.c. of ether and chloroform to remove the last traces of saponified quinine. Wash, dry, and weigh, and in this manner a second quantity of quinine is obtained, which, added to the portion of quinine precipitated in the cold, gives the percentage of the alkaloid present.

Practical Apparatus for the Preparation of Tribromide of Arsenic.—E. Jory.—The author has obtained tribromide of arsenic in a state of purity by the direct action of bromine fumes on arsenic. A matras containing bromine is placed on a water-bath fitted with a cork with two holes and connected through a Welter S-tube with an escape-tube bent in such a manner that the condensed bromine will fall back again into the matras; this tube is connected to a combustion-tube, 2 c.m. in diameter and 15 to 18 c.m. long, containing the arsenic; the other end of this tube is contracted and connected with a flask to receive the tribromide; the second hole is fitted with a glass tube for making communication between the interior of the matras and the air. The matras is gently heated, and when the bromine fumes reach the arsenic, the attack takes place energetically, and owing to the heat generated the tribromide of arsenic is melted and runs into the flask. When cooled it is perfectly white and well crystallised.

No. 8.

On the Filtering Value of old Alluvial Deposits.—F. Malméjac.—Already inserted in full.

Detection of Copper.—A. Bellocq.—If a drop of a solution of sulphate of copper at 1 or 0·5 per cent is allowed to fall into a litre of potable water, and a zincic reagent is added drop by drop until the reaction is strongly alkaline, and the whole is then allowed to stand for four or five hours until it is perfectly limpid, a flocculent precipitate will be formed, varying in appearance from pure white to dirty grey, yellow, or brown, according to the purity of the water. On adding to this precipitate, collected in a small porcelain crucible and dried, a small excess of HCl and then ammonia, the characteristic blue colour of copper is obtained. The sensitiveness of the reaction exceeds the above limits.

MISCELLANEOUS.

Merck's Digest, No. 10.—Cacodylic Acid and Cacodylates.—Cacodylic acid is di-methyl arsenic acid, represented by the formula $As(CH_3)_2O(OH)$. It occurs as oblique rhombic crystals, which dissolve very readily in water and in alcohol, and melt at 200°. Recent investigations have shown that in the form of its salts the toxicity of cacodylic acid is comparatively slight, and hence it is an excellent medium for introducing, without danger, large quantities of arsenic into the human organism. At the same time, ways have been found to avoid the communication of the unpleasant garlic odour to the breath. Cacodylic acid is rarely prescribed as such, but preference is given to the sodium salt; further, the cacodylates of iron, mercury, guaiacol, potassium, calcium, magnesium, lithium, and quinine are contemplated for clinical use. Whether administered internally or injected subcutaneously, cacodylic acid acts as a tonic, and causes no digestive disturbance even when taken in large doses. Its dissociation in the organism is extremely rapid, and the excretion of the ultimate products takes place mainly through the lungs and kidneys.

Preparation of Tetrachloromethane, CCl_4.—E. Serra.—This substance can be obtained absolutely free from CS_2, $CHCl_3$, or S_2Cl_2. Sulphide of carbon is saturated with chlorine in the presence of a little iodine and iron filings; it is then distilled, and the distillate treated with milk of lime in a retort. A brisk reaction takes place, part of the nearly pure product passes over, and the rest is driven over by the help of steam. The dried product is dissolved in a little ICl_3, and heated in a flask fitted with a vertical condenser; hydrochloric acid is given off, and we find free iodine, which is saturated with chlorine until, at the boiling-point, the ICl_3 remains unchanged. The operation is finished by treating with Na_2CO_3 and milk of lime, drying and distilling.—*Gazz. Chim. Ital.*, [II.], vol. xxix., p. 353.

The Chlorisation of *m*-Acet-toluide.—F. Reverdin and P. Crépieux.—By chlorising *m*-acet-toluide by means of chlorate of soda and hydrochloric acid, the authors have obtained a monochlorised, dichlorised, or trichlorised derivative, according to the proportions used; these bodies are fully described.—*Bull. Soc. Chim. de Paris*, Series 3, xxiii., Nos. 20 and 21.

Preparation of Pentachlorophenol.—Et. Barral and L. Jambon.—Pentachlorophenol is very difficult to obtain in a state of purity. It has been prepared by a large number of methods, of which only three are of any value, and they consist in chloridising phenol in the presence of one of the three following bodies:—(1) Chloride of antimony, (2) iodine, (3) anhydrous perchloride of iron. The best conditions are the following:—The chloridising agent must be employed in small quantity, to prevent the formation of tarry matters; it must not be added directly to the phenol at the commencement of the operation, but only when the latter has been converted into trichlorophenol. In spite of the high fusing-point (186°) of pentachlorophenol, it should not be heated above 135—140°, or it may decompose into perchlorodioxydiphenylene and hydrochloric acid, $2C_6Cl_5{\cdot}OH = C_{12}Cl_8O_2 + 2HCl$. The chlorine must be perfectly dry, or tetrachlorised quinone will be formed, $C_6Cl_5.OH + H_2O + Cl_2 = C_6Cl_4O_2 + 3HCl$. By using binoxide of lead, the purification of pentachlorophenol has been made as rapid and perfect as possible. The return, however, is very variable; for, in some cases, with $SbCl_5$ it has been as low as 10 per cent, while with chlorisation in the presence of anhydrous perchloride of iron under the most favourable conditions, as much as 95 per cent of the theoretical return has been obtained.—*Bull. Soc. Chim. de Paris*, Series 3, xxiii., Nos. 20 and 21.

Salts of Thorium.—A. Rosenheim and J. Schilling.—*Chlorides of Thorium.*—On adding aqueous ammonia to a solution of thorium a hydrate is precipitated; this is filtered, washed, and treated with alcoholic HCl. After suitably concentrating the solution small white needles are obtained, which consist of a hitherto unknown oxychloride of thorium corresponding to the formula $Th\begin{matrix}(OH)_2\\Cl_2\end{matrix} + 8H_2O$. The mother-liquor afterwards deposits brilliant crystals, fairly stable in the air. These are shown by analysis to be a chloride of thorium $ThCl_4 + 9H_2O$. If, instead of concentrating the alcoholic solution, the solvent is almost entirely driven off, a syrupy mass remains, which, under the influence of dilute HCl, deposits a fresh oxychloride of thorium in the form of a crystalline powder. This new salt has the formula $Th\begin{matrix}OH\\Cl_3\end{matrix} + 11H_2O$. By mixing alcoholic solutions of chloride of thorium and hydrochlorate of pyridine, the authors have obtained a well-crystallised double salt $(C_5H_5N)_2H_2ThCl_6$. *Bromides of Thorium.*—The hydrate of thorium is treated with HBr, and the alcoholic solution slowly evaporated. This latter then deposits, in the form of small quadratic crystals, an oxybromide $Th\begin{matrix}(OH)_2\\Br_2\end{matrix} + 11H_2$, analogous to the preceding oxychloride. In this case there is also formed a tetrabromide of thorium, $ThBr_4 + 7H_2O$, which crystallises in well formed colourless needles. These latter are not very stable, but decompose rapidly in the air, losing HBr. By reacting with bromide of thorium and hydrobromate of pyridine in alcoholic solution a double salt is also formed of the composition $(C_5H_5N)_2H_2ThBr_6$. This compound, easily soluble in water and in absolute alcohol, changes rapidly when exposed to the air, taking an intense yellow colour. The authors propose to continue this research, and will examine the preparation and properties of the oxides and sulphates of thorium.—*Berichte*, xxxiii., p. 977.

Some Chlorarates of Organic Bases with Abnormal Compositions.—G. Fenner and J. Tafel.—Piperidine gives two chlorarates; the normal salt $C_5H_{12}NAuCl_4$ always forms in aqueous solution; it is stable, and may be re-crystallised in alcohol and water. The abnormal salt, $(C_5H_{12}N)_2AuCl_5$, forms exclusively in alcoholic solution, or when the normal solution is treated with an alcoholic solution of hydrochlorate of piperidine or simply hydrochloric gas. On the other hand, the normal salt is regenerated when it is treated with water, in the cold, or when its alcoholic solution is heated, $(C_5H_{12}N_2)AuCl_5 = C_5H_{12}N.AuCl_4 + C_5H_{12}NCl$. Other bases form abnormal chlorarates which have practically the same properties, while methylamine, aniline, pyridine, and conicine give none. *Piperidine.*—The normal salt crystallises in water in flakes, fusible at 218—229° with decomposition; it is soluble in alcohol and water. It is dissociated in warm alcoholic solution. The abnormal salt, prepared in alcoholic solution with chloride of gold, is slightly soluble in alcohol; it is a yellow, crystalline powder, fusible at about 197°, giving off hydrochloric gas. The reciprocal transformation of the two salts takes place as has been shown above. *Isopropylamine.*—The abnormal salt consists of a microcrystalline yellow powder, fusible at about 159°, soluble in alcohol. The normal salt is in yellow tables, fusible at 131—135°. *Au-methylpiperidine.* The normal salt melts at about 96—100°, and the abnormal salt at about 102—104°. It occurs in yellow flakes. *Quinolein.*—The abnormal salt melts at 180°, and decomposes about 260°. The normal salt melts at 235—238°, and decomposes likewise at 260°. The *Chlorauvate of Pyridine*, $C_5H_6NAuCl_4$, is slightly soluble in boiling alcohol (1 in 60). That of methylamine is decomposed into hydrochlorate by ether in the presence of hydrochloric gas.—*Berichte*, vol. xxxii., p. 3220.

MEETINGS FOR THE WEEK.

MONDAY, 25th.—Society of Arts, 8. (Cantor Lectures). "Electric Railways," by Major Philip Cardew, R.E., &c.

TUESDAY, 26th.—Royal Institution, 3. "The Cell as the Unit of Life," by Allan Macfadyen, M.D., B.Sc.

—— Society of Arts, 8. "The Commonwealth of Australia," by The Hon. Sir John Alexander Cockburn, K.C.M.G.

WEDNESDAY, 27th.—Society of Arts, 8. "Clocks, Carillons, and Bells," by A. A. Johnston.

THURSDAY, 28th.—Royal Institution, 3. "Shakespeare in Relation to His Contemporaries in Art," by Sir Wyke Bayliss, F.S.A.

—— Society of Arts, 4.30 (at the Imperial Institute, South Kensington). "The Greek Retreat from India," by Colonel Sir Thomas Hungerford Holdich, R.E., K.C.I.E., C.B.

—— Chemical, 3. (Annual General Meeting).

FRIDAY, 29th.—Royal Institution, 9. "Polish," by Lord Rayleigh, F.R.S., &c.

SATURDAY, 30th.—Royal Institution, 3. "Sound and Vibrations," by the Rt. Hon. Lord Rayleigh, F.R.S., &c.

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THE CHEMICAL NEWS.

VOL. LXXXIII., No. 2157.

ON THE PREPARATION OF LARGE QUANTITIES OF TELLURIUM.*

By EDWARD MATTHEY, A.R.S.M.

FOR several years I have worked upon bismuth ores of varying richness for the extraction of the bismuth they contain, and I have already communicated the results to the Royal Society (*Roy. Soc. Proc.*, 1887, vol. xlii., p. 89; 1890, vol. xlix., p. 78; and 1893, vol. lii., p. 467). Many, if not most of these ores, contain traces of tellurium.

Tellurium has a marked tendency to associate itself with bismuth, as silver may be said to do with lead, or phosphorus with iron, and accordingly the crude bismuth extracted from these ores invariably contained small quantities of tellurium, which was reduced together with the bismuth, and was found to exist in it in a greater proportion than in the ores.

The presence of even minute traces of tellurium in bismuth being sufficient to render this metal unsaleable, it is necessary to remove every portion of the tellurium whilst refining the crude bismuth. The alkalis containing the tellurium resulting from the refining of the crude bismuth were thrown aside, and were left for future investigation.

I have now been able to treat these alkaline residues, and have extracted from them a substantial amount of metallic tellurium, weighing 26 kilos. This amount of tellurium was produced from 321 tons of mineral containing an average amount of 22·50 per cent of bismuth.

The amount of metallic tellurium obtained corresponds to an average of 0·007 per cent of the original mineral.

The 26 kilos. of metallic tellurium was obtained by soaking the telluride alkalis, resulting from refining the telluric bismuth in hot water—acidifying these solutions with hydrochloric acid, and precipitating the tellurium with sodium sulphite. A crude mixture of bismuth and tellurium was thus obtained, the tellurium forming about 47·5 per cent of the crude metal.

This was dissolved in nitric acid, and again treated in the same way, and yielded the amount of tellurium represented by the 26 kilos. This shows on analysis:—

Tellurium	97·00
Bismuth	2·15
Copper	0·65
Iron	0·10
Loss	0·10
	100·00

The appearance of the metal when broken shows a crystalline fracture, of needle-like structure, and of bright metallic lustre. It does not readily tarnish in the air at the ordinary temperature. If slowly cooled, a crystalline form very much resembling that of bismuth is obtained.

Its specific gravity is 6·27, as against 6·23, the density of uncompressed tellurium found by Spring.

The temperature of solidification was determined by means of the Le Chatelier pyrometer, and proved to be 450° C., or 5° lower than that given by Carnelley and Williams (*Chem. Soc. Journ.*, vol. xxxvii., p. 125).

Some tellurium prepared from this 26 kilos. to chemical purity also gave 450° C. as the solidifying point.

Commercial tellurium obtained from Germany proved to have the same melting-point and specific gravity as my own tellurium.

I found the electrical resistance to be about 800 times that of copper. The resistance, however, appears to be very greatly dependent on the crystalline conditions.

A rod cast and cooled quickly has a lower resistance than one that has been cooled slowly. A current of a few ampères will quickly raise the temperature of a rod 0·2 inch in diameter. In casting small rods of tellurium, of, say, ⅜ inch diameter, there is much contraction, and partial separation takes place even after some hours.

The thermo-electric power of tellurium appears to be great.

It has been a source of great satisfaction to me, as a metallurgist, to produce so large an amount of tellurium from a mineral in which it existed only in minute traces. The amount of 57½ lbs. (26 kilos.) of tellurium was derived from 187,019 lbs. of crude bismuth, which resulted from the treatment of 831,168 lbs. of mineral.

* A Paper read before the Royal Society, March 14, 1901.

SOME PHYSICAL PROPERTIES OF NITRIC ACID SOLUTIONS.*

By V. H. VELEY, F.R.S., and J. J. MANLEY,
Daubeney Curator, Magdalen College, Oxford.

THE results obtained by the authors on the electric conductivity of solutions of nitric acid have led them to continue their investigations on other physical properties of the same substance with a view of confirming the conclusions drawn therefrom.

In the present paper the properties examined are the densities, with especial reference to the contractions, and the refractive indices.

The various sources of error and their possible magnitude are discussed in full; for the densities, those of analysis, unavoidable in this case, temperature, errors of filling pyknometers both with acid and water; for the refractive indices, those of micrometer screws, divided circle, parallelism of quartz plates are more especially alluded to, as also the several effects likely to be produced by the various substances with which the acid solutions of necessity came into contact. The results obtained by both methods are given in a series of tables, and compared with those calculated from various equations for straight lines. These show that the physical properties are discontinuous at points corresponding very approximately to the concentrations required for simple molecular combinations *only* of nitric acid and water. In the case of the densities and contractions, the best defined points of discontinuity correspond to the composition of the hydrates with 14, 7, 4, 3, 1·5, and 1 molecular proportions of water; in the case of the refractive indices, the most marked points correspond to the 14, 7, and 1·5 hydrates.

The results for the contractions further confirm those for the electric conductivities as to a remarkable discontinuity at concentrations 95 per cent to 100 per cent, which can possibly be explained by some cause other than the combination of acid with water.

The contractions show that these points of discontinuity, though to some degree real, yet to another degree are ideal in that there is within the limits of 1 to 2 per cent in the vicinity of such points a transition stage.

The values for μ are further expressed in terms both of Gladstone and Dale's and of Lorentz's formula, and it is shown that the values in neither case are constant, but decrease with increase of concentration, and also that Pulfrich's formula which expresses the relation between the refractive index and the contraction in terms of a constant is only approximately applicable for results differing by small percentage concentrations, but not so in the case of considerable differences.

The results are illustrated by a selection of curves, with especial reference to the points of discontinuity.

* Abstract of a Paper read before the Royal Society, March 7th, 1901.

QUANTITATIVE DETERMINATION OF SCAMMONY FOR COMMERCIAL PURPOSES.

By P. L. ASLANOGLOU.

To a weighed quantity of scammony add some ether and gently warm, to dissolve quicker; let it stand to settle, and filter through some cotton-wool; to the residue add some more ether, and repeat as above three times. All earthy and insoluble matter will remain in the filter. Wash well the cotton-wool with warm ether, and to the filtrate add enough turpentine, and let it stand for some hours, when a globular oily-looking precipitate will be found to settle down in the ether-turpentine mixture, consisting solely of scammony; any admixture of other gum-resins will be kept in solution by the ether-turpentine mixture; the scammony, being insoluble in turpentine, precipitates. Decant the ether-turpentine mixture, wash precipitated scammony with fresh turpentine only, evaporate gently on a water-bath, and weigh; thus one has the commercial value of scammony in samples. To estimate the earthy insoluble matters, the cotton-wool filter should be dried with its contents in a water-oven, burned, and weighed; of course, the ash of cotton-wool per grm. used should be known. The ether-turpentine mixture, evaporated and weighed, will give the amount of foreign gum-resins.

ON OXIDE OF BISMUTH.

By M. PAUL THIBAULT.

Commercial oxide of bismuth always contains a certain proportion of nitric acid; it therefore appeared to be of interest to examine its precipitation with a view to obtaining the hydrate of oxide of bismuth free from acid.

The methods given by Carnelley and Walker, Muir and Carnegie, and Arpe were tried, and all gave oxides containing nitric acid, as also did that of M. Baudran. However, the oxide obtained by this latter method contained a little less nitric acid (about 0·5 per cent less in HNO_3) than those obtained by the previous methods.

We therefore made use of this method, working at different temperatures, the temperature varying by 10° at a time, from 0° to 100°. The quantities of nitric acid found varied from 2 to 5 per cent; the smallest amount being found at 0°, and the greatest at 100°.

By using the halogen salts of bismuth instead of the nitrate our results were of a similar character.

By using potash instead of ammonia in these last experiments the proportion of hydrochloric acid was diminished.

M. Baudran has stated that contact with the alkali, far from destroying the sub-salt, increased its proportion. We verified this fact and found that a precipitate of oxide of bismuth, giving 3·45 per cent of acid when washed immediately, contained 6·20 per cent after three days, and 9·40 per cent after twenty days, or an increase of about 5 per cent of acid in twenty days.

The idea then occurred to us to precipitate the oxide of bismuth from an alkaline solution by means of an acid, instead of precipitating the acid solution by an alkali, profiting by the known property of oxide of bismuth of dissolving in potash in the presence of glycerin. This solution is precipitated by sulphuric acid.

The oxide obtained in this manner contains neither nitric nor sulphuric acids.

We commence by dissolving crystallised nitrate of bismuth in water in the presence of glycerin; we then add a solution of potash containing enough alkali to form an excess; we then saturate with dilute sulphuric acid, taking care not to add too much acid; for this purpose it is perhaps better to leave the solution with a slight alkaline reaction.

In this manner we obtain a white gelatinous product, which can be preserved in this state provided it is kept in water; it does not change on exposure to light. Even after prolonged washing with cold water it still retains small quantities of potash; when submitted to desiccation it becomes transformed into a greyish-white powder of a composition answering to the formula $Bi_2O_3.H_2O$.

To determine its composition we analysed three samples, each dried in a different manner:—

1. *In Dry Air.*

	Found. I.	Found. II.	Calculated for $Bi_2O_3.H_2O$.
Bi_2O_3	95·47	95·08	96·30
H_2O..	4·53	4·92	3·70

2. *In Sulphuric Vacuo.*

	Found. I.	Found. II.	Calculated for $Bi_2O_3.H_2O$.
Bi_2O_3	95·95	95·98	96·30
H_2O..	4·05	4·02	3·70

3. *In the Oven at* 100—105°.

	Found. I.	Found. II.	Calculated for $Bi_2O_3.H_2O$.
Bi_2O_3	96·36	96·04	96·30
H_2O..	3·64	3·96	3·70

Thus, by our method, we are able to obtain a hydrate of oxide of bismuth free from acid, and capable of preserving its gelatinous state, by precipitating the oxide from its alkaline solution by an acid, instead of precipitating it from its acid solution by an alkali.—*Bull. Soc. Chim.*, Series 3, vol. xxv., No. 3.

ALCOHOLATES OF ALUMINIUM. THEIR PROPERTIES AND THEIR REACTIONS.

By V. TISTCHENKO.

A current of dry hydrochloric acid decomposes the ethylate of aluminium with evolution of heat; this body changes into a brown liquid which solidifies on cooling. The reaction is fairly complex; there is not only alcohol and chloride of aluminium formed, the proportion of chlorine in the solid residue is lower than that corresponding with $AlCl_3$. The isobutylate and the isopropylate in solution in perchloride of carbon, treated with dry HCl, and kept either at the temperature of the laboratory or at 0° C., gave the reaction $Al(OR)_3+3HCl=AlCl_3.3ROH$. These solid compounds of $AlCl_3$ with the isopropylic and isobutylic alcohols are very hygroscopic; water decomposes them, forming alcohols.

With the halogen derivatives of the saturated carbides ethylate of aluminium does not form simple or mixed ether oxides, even when heated in sealed tubes; the experiment was tried with iodide of ethyl, bromide of ethyl, and chloroform. Neither does the isopropylate react with C_2H_5I at 100°; there is a certain reaction at 170—180°, but ether oxide is not formed.

Under the direction of the author, M. Gabounia treated the isopropylate of aluminium with dibromopropylic alcohol produced by the union of Br_2 with allylic alcohol; he obtained the following reaction:—

$$Al(C_3H_7O)_3+3CH_2Br\,CHBr.CH_2OH = Al(CH_2Br.CHBr.CH_2O)_3+3C_3H_7OH.$$

Dibromopropylate of aluminium forms a viscous colourless mass, absorbing moisture with rapidity, and decomposed by water into Al_2O_3 and dibromopropylic alcohol. Ethylate of aluminium reacts slowly in the cold on chloride of acetyl, but more rapidly on the water-bath, giving $AlCl_3$ and acetate of ethyl, but the return is far from the theoretical amount.

The author and his pupils have examined the action of some anhydrides on the alcoholates of aluminium; this action is of interest as it enables us to obtain salts of weak acids and aluminium.

Ethylate of aluminium with acetic anhydride gives acetate of ethyl and neutral acetate of aluminium; this body occurs as a white powder soluble in water; the solution does not become cloudy on boiling, but the addition of acetate of soda gives an abundant precipitate.

$Al(C_2H_3O_2)_3$ decomposes above 200° C., giving off CO_2, acetone, and acetic acid. A prolonged current of CO_2 over ethylate of aluminium moistened with benzene gives a colourless, semi-transparent mass, which is the salt $Al(CO_3C_2H_5)(OC_2H_5)_2$. In an analogous manner SO_2 gives the compound $Al(OSO.C_2H_5)_2(OC_2H_5)$.

The author and his pupils have also examined the decomposition of the alcoholates of aluminium by heat, besides examining the decomposition by heat of a number of alcohols, ether oxides, and aldehydes.—*Journ. Soc. Phys. Chim. R.*, vol. xxxi., p. 784.

ON THE COMPLEX SALTS OF PLATINUM. ALKALINE-EARTHY OXALONITRITES.

By M. VÈZES.

The platino-oxalonitrite of potassium,

$$Pt(C_2O_4)(NO_2)_2K_2+H_2O,$$

of which the preparation and principal properties have already been described (*Bull. Soc. Chim.*, Series 3, vol. xxi., p. 481; Chemical News, vol. lxxx., p. 63), serves as the starting point in the preparation of these new salts, also derived from a platino-oxalonitrous acid, which can be formulated thus:—$Pt(C_2O_4)(NO_2)_2H_2$.

I propose in this paper to examine the reactions by which alkaline-earthy platino-oxalonitrites can be formed in a similar manner.

1. *Action of Chloride of Barium on Platino-oxalonitrite of Potassium.*—When we make a solution of chloride of barium react on a solution of platino-oxalonitrite of potassium, we obtain reactions which are very different according to the conditions under which the operation is performed.

If we operate in the cold, using 1 molecule of chloride of barium for each molecule of platino-oxalonitrite, each salt being dissolved in the smallest possible amount of water, we obtain an abundant golden-yellow crystalline deposit in a few moments. The analysis of these crystals, of which the results are given below, leads to the formula $Pt(C_2O_4)(NO_2)_2Ba+5H_2O$, or a platino-oxalonitrite of barium. The double decomposition in cold solution, which has given rise to this new salt, has thus consisted of a change of metals between the two reacting salts; it can be represented by the equation:

I. $Pt(C_2O_4)(NO_2)_2K_2+BaCl_2=Pt(C_2O_4)(NO_2)_2Ba+2KCl.$

If we mix the same solutions boiling, containing the same relative quantities of the two reacting salts, we observe that the mixture rapidly becomes cloudy, giving a white crystalline precipitate. The analysis of this precipitate shows that it is free from platinum; it is the hydrated oxalate of barium, C_2O_4Ba,H_2O, containing 56·98 per cent Ba; calculated, 56·45. The whole of the barium used in the state of chloride being thus precipitated in the form of oxalate, the supernatant liquid is a solution of platinodichloronitrite of potassium, $PtCl_2(NO_2)_2K_2$, which can be obtained in the crystalline state after sufficient concentration. The double decomposition, effected in boiling solution, has thus consisted of a change between the groups CO_2 of the oxalonitrite and the atoms of chlorine of the chloride of barium; it can be represented by the equation:—

II. $Pt(C_2O_4)(NO_2)_2K_2+BaCl_2=PtCl_2(NO_2)_2K_2+C_2O_4Ba.$

Finally, we can get a third reaction, different to both the preceding ones, if we modify the proportions in which the two salts are made to react; by using only a demi-molecule of chloride of barium for each molecule of platino-oxalonitrite of potassium, and by operating in the cold, we observe the production of a yellow solution, which first remains perfectly limpid, and then after a few hours forms small yellowish-brown prisms, of a deeper colour than the platino-oxalonitrite of barium or the platino-oxalonitrite or platinodichloronitrite of potassium. The analysis of these crystals (see below), leads us to look upon them as a mixed platino-oxalonitrite of barium and potassium; they correspond in fact to the formula:—

$$Pt_2(C_2O_4)_2(NO_2)_4BaK_2,4H_2O=$$
$$=Pt(C_2O_4)(NO_2)_2Ba,Pt(C_2O_4)(NO_2)_2K_2,4H_2O,$$

and result from a reaction analogous to No. I., but in which the change of metals has only been partial:—

III. $2Pt(C_2O_4)(NO_2)_2K_2+BaCl_2=$
$$=Pt_2(C_2O_4)_2(NO_2)_4BaK_2+2KCl.$$

This reaction is also produced without the precipitation of barytic oxalate, if we mix warm solutions (80°) of the two salts in the proportions given above. The precipitate of barytic oxalate only appears if we operate at a boiling temperature, and even then it only occurs with a small portion of the barium present, so that the filtrate will still give a good return of barytopotassic-platino-oxalonitrite. In this case the mother-liquor, concentrated in its turn, gives a deposit of platinodichloronitrite of potassium, resulting, like the barium oxalate first obtained, from the reaction (II.) effected on a part of the reacting mixture.

The two new salts which have just been described, platino-oxalonitrite of barium and platino-oxalonitrite of barium and potassium, form a series with platino-oxalonitrite of potassium,

$$Pt(C_2O_4)(NO_2)_2Ba+5H_2O,$$
$$Pt_2(C_2O_4)_2(NO_2)_4BaK+4H_2O,$$
$$Pt(C_2O_4)(NO_2)_2K_2+H_2O,$$

which does not admit of any other term.

If, in fact, we cause chloride of barium and platino-oxalonitrite of potassium to react in any other proportions than those given above, we do not obtain new salts, but mixtures of the preceding ones; for example, the action of 1 molecule of platino-oxalonitrite of potassium on less than half a molecule of chloride of barium gives very plainly a deposit of the barytopotassic salt, quickly followed by a second crystalline deposit of a much lighter colour, and which is nothing else than the excess of the potassium salt used.

These results collectively should apparently be interpreted as follows:—The platino-oxalonitrite of barium, formed by the reaction I., is the normal product of the action of chloride of barium on platino-oxalonitrite of potassium. But it decomposes in aqueous solution, slowly in the cold and rapidly on boiling, with a deposit of hydrated oxalate of barium; in the presence of a chloride this deposit is accompanied by the formation of a platinodichloronitrite (reaction II.). This decomposition is facilitated by the presence of an excess of chloride of barium or potassium; on the other hand, it is retarded by the presence of an excess of platino-oxalonitrite of potassium; but, in the latter case, the barium salt, thus rendered more stable, becomes united to the excess of the potassium salt, and forms a mixed baryto-potassic salt (reaction III.).

2. *Platino-oxalonitrite of Barium.*—The examination which has just been described of the possible reactions between platino-oxalonitrite of potassium and chloride of barium leads, as far as it concerns the platino-oxalonitrite of barium, to the following method of preparation, which has been used for obtaining considerable quantities of this salt (about 200 grms.), which were necessary for the preparation of other oxalonitrites.

The platino-oxalonitrite, which is the starting-point of

this preparation, is obtained by the method already described (*loc. cit.*), with one single modification. With a view to increasing the yield of the operation, the yellow liquor containing the salt is evaporated down before cooling, so as to reduce its volume from 2 litres to about half a litre. Thus we immediately obtain 180 grms. of the salt instead of 160 grms. without interfering with its purity, while still starting with 200 grms. of the hydrated platinonitrite; the theoretical return is 190 grms., and not 210 grms. as was previously stated by mistake (*loc. cit.*).

The reaction it is desired to produce between the two solutions should take place in the cold, and as the platino-oxalonitrite of potassium is only slightly soluble in cold water the amount of material employed is limited by the volume of the solution in use. For each operation I used 70 grms. of the pure salt; this was dissolved in boiling water (about a litre), and then diluted with cold water, bringing the total volume to 5 litres. After completely cooling, 150 c.c. of a cold solution of chloride of barium, containing 1 molecule of the salt per litre, was poured slowly in with constant stirring. The solution, which is first of a pale yellow colour, becomes darker, and a crystalline deposit of platino-oxalate of barium is slowly formed. This deposit is complete in a few hours: if we wait too long we observe white patches of oxalate of barium appear on the golden-yellow crystals of the salt; this is caused by the decomposition of the portion still remaining in solution.

After decanting and draining the crystals left, they are re-dissolved as rapidly as possible in about a litre of boiling water. There is still a slight deposit of oxalate of barium formed in this operation; it is separated by filtration, and the filtrate left to cool. The platino-oxalonitrite of barium crystallises immediately, and this time is perfectly pure; it is collected rapidly and dried between filter-paper. In this way, starting with the above mentioned weight of material, 62 grms. of the pure crystallised salt are obtained; theory requires 90 grms. The missing 28 grms. exist partly in the 5 litres of the mother-liquor from the double decomposition, and partly in the litre of mother-liquor from the re-crystallisation; but their extraction in the form of the barium salt is impossible, the prolonged evaporation it has been necessary to submit these 6 litres of liquid to, having had the effect of precipitating all the barium in the form of oxalate, while the platinum has passed into the state of platinodichloronitrite of potassium (reaction II.). We might therefore make use of this transformation to prepare this platinodichloronitrite from residues. It is, however, better to add an excess of oxalate of potassium to the boiling mother-liquors. This transforms the platinodichloronitrite into platino-oxalonitrite of potassium, which is much less soluble, and therefore much easier to collect by cooling. We also recover practically all the potassium salt which has not been used in the reaction.

Platino-oxalonitrite of barium occurs in the form of golden-yellow crystals; under the microscope these crystals generally appear as elongated parallelograms, of which the acute angle is about 68°; they act on polarised light, and have a position of extinction parallel to one of the sides of the parallelogram. When dried in the cold between blotting-paper these crystals do not change in the air.

They contain 5 molecules of water of crystallisation, which they lose with difficulty when heated; ten days in an oven at 110—120° are not sufficient to dehydrate them completely. It is only at about 200° after several hours that their dehydration can be effected.

The examination of this dehydration denotes the probable existence of at least two distinct hydrates, of which it will be of interest to estimate the saturated vapour tension. We observe, in fact, that on gradually heating a sample of the salt it commences to effloresce at about 70°, and at the same time its colour changes to cinnabar-red; this gradually becomes deeper and deeper until it is almost black. A weighing made at this moment shows that the salt has lost nearly three molecules of water out of the five. On continuing the dehydration the colour becomes less deep again, changing first to bright red, and then to bright orange-red; it finally becomes orange-yellow, and ceases to lose water; the dehydration is then complete.

If the temperature is then raised to 275° we see an altogether different phenomenon analogous to that already described (*loc. cit.*) for platino-oxalonitrite of potassium. The salt decomposes rapidly with considerable swelling up, but with no projections; it becomes completely black, the platinum being set free. But while the decomposition of the potassium salt was accompanied with a disengagement of carbonic acid gas, the potassium remaining in the state of nitrite according to the equation $Pt(C_2O_4)(NO_2)_2K_2 = Pt + 2NO_2K + 2CO_2$, the barium salt, on the contrary, decomposes with the evolution of nitrous fumes, the barium remaining in the state of oxalate (sometimes partly transformed into carbonate, with the evolution of carbonic oxide, as shown by the figures quoted below of the analysis of the salt). This decomposition should therefore be expressed—

$$Pt(C_2O_4)(NO_2)_2Ba = Pt + C_2O_4Ba + 2NO_2.$$

Platino-oxalonitrite of barium is soluble in ten times its weight of boiling water, and in forty times its weight of cold water. This solubility, as well as the facility with which it is prepared, renders it valuable for the preparation of other oxalonitrites by double decomposition with the metallic sulphates. But these solutions are not very stable; very slowly in the cold, and more rapidly when boiling, they deposit crystallised oxalate of barium.

The analysis of platino-oxalate of barium was done by the same methods as were used for the potassium salt except for the estimation of the metals; this dehydrated salt is decomposed at 275°, and then heated to redness, which transforms the oxalate into carbonate; the residue is washed with dilute hydrochloric acid; the remaining platinum is weighed, and the barium in the filtrate estimated as sulphate. In this manner we obtained the following results:—

I. 0·6334 grm. of material, heated to 160°, lost 0·0926 grm. of water. The dry residue, heated to redness, weighed 0·4120 grm.; after washing with dilute hydrochloric acid it gave 0·2047 grm. of platinum, and 0·2247 grm. of sulphate of barium, containing 0·1440 grm. of barium.

II. 0·7200 grm. of material, heated to 200°, lost 0·1085 grm. of water. The dry residue, after decomposition at 275°, weighed 0·4938 grm.; after calcination at a red heat it weighed 0·4639 grm. When treated as before it gave 0·2743 grm. of sulphate of barium, containing 0·1614 grm. of barium.

III. 0·4454 grm. of material, treated in the same manner, gave 0·1442 grm. of platinum.

IV. 0·5803 grm. of material, heated to 200°, lost 0·0857 grm. of water. The dry residue, heated to redness, weighed 0·3766 grm. After washing with dilute hydrochloric acid it gave 0·1879 grm. of platinum, and 0·2180 grm. of sulphate of barium, containing 0·1283 grm. of barium.

V. 0·5056 grm. of material, after decomposition at 275°, gave a residue weighing 0·3474 grm.; after heating to redness, a residue of 0·3303 grm. and after calcination with an excess of sulphuric acid a residue of 0·3605 grm.

3. *Baryto-potassic Platino-oxalonitrite.* — This salt, which is obtained in the manner already described, occurs in the form of small brownish-yellow prisms. Under the microscope its crystals have the appearance of elongated rectangles; they act on polarised light, and their positions of extinction are parallel to the sides of the rectangle. When dried in the cold between filter-papers these crystals do not change in the air.

With regard to the action of heat, their properties are analogous to those which have been described for the normal barium salt. Like the latter the baryto-potassic salt is difficult to dehydrate, and gives rise to very marked changes of colour; at about 253° it decomposes with

TABLE I.

	Calculated.		Found.				
			I.	II.	III.	IV.	V.
Pt	194·8	32·34	32·32	—	32·38	32·38	—
Ba	137·4	22·81	22·73	22·42	—	22·11	—
2C	24·0	3·98	—	—	—	—	—
2N	28·1	4·67	—	—	—	—	—
8O	128·0	21·24	—	—	—	—	—
$5H_2O$	90·1	14·96	14·62	15·07	—	14·77	—
$Pt(C_2O_4)(NO_2)_2Ba.5H_2O$	602·4	100·00	—	—	—	—	—
$3H_2O$	54·1	8·98	9·16	—	—	9·20	—
$Pt+C_2O_4Ba$	420·2	69·76	—	68·58	—	—	68·71
$Pt+CO_3Ba$	392·2	65·11	65·05	64·43	—	64·91	65·33
$Pt+SO_4Ba$	428·3	71·10	—	—	—	—	71·30

TABLE II.

	Calculated.		Found.			
			I.	II.	III.	IV.
Pt	194·8	37·55	37·14	37·09	—	—
K	39·1	7·54	8·27	7·97	—	—
½Ba	68·7	13·25	14·0	13·80	13·57	—
2C	24·0	4·63	—	—	—	4·80
2N	28·1	5·42	—	—	—	5·07
8O	128·0	24·67	—	—	—	—
$2H_2O$	36·0	6·94	—	6·99	—	—
$\frac{1}{2}[Pt_2(C_2O_4)_2(NO_2)_4BaK_2.4H_2O]$	518·7	100·0	—	—	—	—
$\frac{1}{2}[Pt_2+CO_3Ba+CO_3K_2]$	362·6	69·91	—	—	69·89	—
$\frac{1}{2}[Pt_2+CO_3Ba]$	293·5	56·58	57·28	—	—	—

efflorescence, giving off nitrous fumes, leaving a residue of platinum and oxalates of barium and potassium—

$Pt_2(C_2O_4)_2(NO_2)_4BaK_2 = 2Pt + C_2O_4Ba + C_2O_4K_2 + 4NO_2$.

This manner of decomposition, in which the baryto-potassic salt behaves quite differently to a mixture of the salt of barium with that of potassium (see above), is of special importance, since it furnishes proof of the individuality of the salt. Beyond this its colour, which is much deeper than that of the salt of barium or potassium, is also sufficient to exclude the hypothesis of a simple mixture, and its proportion of water of crystallisation, which, as has been shown, is not the mean of that of these two salts, further confirms this conclusion.

The solubility of baryto-potassic platino-oxalonitrite in water appears to be a little higher than that of the normal barium salt. Its analysis has given the following results:

I. 0·3584 grm. of material, after calcination at red heat and washing with water, left a residue (Pt and CO_3Ba), of 0·2053 grm.; the washings, evaporated to dryness with sulphuric acid, gave 0·0660 grm. of sulphate of potassium, containing 0·0297 grm. of potassium; the residue, treated with dilute hydrochloric acid, gave 0·1331 grm. of platinum, and 0·0859 grm. of sulphate of barium, containing 0·0505 grm. of barium.

II. 0·6096 grm. of material, heated to 220°, lost 0·0426 grm. of water. The dry residue, after digestion with hydrochloric acid, gave 0·2261 grm. of platinum, 0·0926 grm. of chloride of potassium containing 0·0486 grm. of potassium, and 0·1430 grm. of sulphate of barium containing 0·0841 grm. of barium.

III. 0·5411 grm. of material, after calcination at red heat, left a residue (platinum and carbonates of barium and potassium) weighing 0·3782 grm.; its treatment with dilute hydrochloric acid, and then with sulphuric acid, gave 0·1248 grm. of sulphate of barium containing 0·0734 grm. of barium.

IV. 0·4344 grm. of material, heated to redness with excess of tungstic acid, gave 17·6 c.c. of nitrogen at 760 m.m., weighing 0·0220 grm., and 38·9 c.c. of carbonic acid, weighing 0·0764 grm. and containing 0·0208 grm. of carbon.

4. *The Case of Strontium and Calcium.*—Experiments analogous to those which have been described were made with the chlorides of strontium and calcium. The action of these salts on platino-oxalonitrite of potassium appears to be analogous to that of chloride of barium; at first the liquid becomes strongly yellow. But, even when operating in the cold, we cannot here prevent the appearance, a few moments after mixing, of the alkaline-earthy oxalate precipitate which denotes that Reaction II. has taken place; that is to say, the destruction of the platino-oxalonitrite of strontium or calcium, apparently formed in the first instance, and too soluble to be deposited without previous concentration. Further, this precipitation of strontium or calcium in the form of oxalate is soon finished, especially if we concentrate the mixture by evaporation with a view of obtaining a mixed oxalonitrite. All the platinum passes into the state of platinodichloronitrite of potassium, so that it has not been possible up to the present to obtain salts of strontium and calcium analogous to the salts of barium which have just been described, on account of the instability of their aqueous solutions.—*Bull. Soc. Chim.*, Series 3, vol. xxv., No. 3.

A New Glucoside, Methylene-glucose, obtained with Glucose, Formic Aldehyde, and Hydrochloric Acid.—B. Tollens.—500 grms. of glucose, 500 grms. of formic aldehyde at 40 per cent, 50 grms. of concentrated hydrochloric acid, and 50 grms. of acetic acid are left together in contact for several months; the crystals obtained crystallise in boiling water in needles, and have the formula $C_{10}H_6(CH_2)O_6.\frac{1}{2}H_2O$. This molecule of water goes off at 100°. The body melts at 187—189°, previously softening at 180°, $(\alpha)_D = +9·3°$; it reduces Fehling's solution, absorbing $1\frac{1}{2}O$, while glucose absorbs $2\frac{1}{2}O$. Its osazone, $C_{19}H_{22}N_4O_4$, is a yellow powder, fusible at 164—166°, after softening at 160°. Methylene glucose does not ferment with brewers' yeast; it gives a yellow precipitate with phloroglucine and hydrochloric acid.—*Berichte*, vol. xxxii., p. 2585.

SOME PRINCIPLES AND METHODS OF ROCK ANALYSIS.*

By W. F. HILLEBRAND.

(Continued from p. 138).

VIII. *Aluminum. Total Iron. Indirect Method for Aluminum.*

THE common practice in this laboratory is to find alumina by difference, after deducting from the precipitate produced by ammonia or sodium acetate the sum of all other oxides this precipitate may contain. Of these, only ferric oxide, titanic oxide, and the trace of silica are determined in this portion (see also last footnote, next column), those of phosphorus, vanadium, chromium, and zirconium being looked for in other portions of the rock powder. This throws upon the alumina all errors involved in their separate determinations; but these may balance, and in any case the probable error can hardly be as high as that involved in the direct weighing of the alumina itself, considering the difficulty of effecting a satisfactory separation of it from all the other admixtures—an operation which would, moreover, immoderately extend the time required for each analysis.

Precipitation of Aluminum, Iron, &c.

Precipitation by Ammonia.—Two precipitations by ammonia at boiling heat are usually quite sufficient to separate iron, aluminum, phosphorus, vanadium, chromium, titanium, and zirconium, if all these are present, from nickel, manganese, the alkaline-earth metals, and magnesium, provided ammoniacal salts are present in sufficient quantity. This last point is of special importance as regards magnesium, and failure to observe it is doubtless the reason why many old analyses, and sometimes modern ones, show utterly improbable percentages of alumina, especially as chemists were formerly often satisfied with a single precipitation. The necessary ammonium chloride is better obtained by the use of purified ammonia water and hydrochloric acid than by the addition of the solid salt, which is seldom pure.

Precipitation by the Basic Acetate Method.—But it will occasionally happen that the separation from even very small amounts of manganese is altogether incomplete, and the uncertainty of ensuring this separation has led the writer of late to employ the basic acetate method for the first precipitation in all cases where manganese is present—and the exceptions are few—even though the precipitation of alumina is sometimes less complete than by ammonia, and in spite of other admitted defects, as, for instance, a tendency of the precipitate to run through the filter on washing.† Not more than 2, or at most 3, grms. of sodium acetate need be used. After slight washing and sucking dry at the pump, the precipitate is re-dissolved in a large excess of hydrochloric acid and re-precipitated by ammonia in slight excess. The complete boiling off of this excess is unnecessary, as pointed out by Genth and Penfield, since it is apparently the washing with pure water and not the free ammonia which carries small amounts of alumina into the filtrate. Penfield and Harper (*Am. Journ. Sci.*, 1886, Series 3, vol. xxxii., p. 112) recommend washing with a dilute solution of ammonium nitrate (20 c.m.³ nitric acid, neutralised by ammonia, to the litre), and also the solution of the first precipitate in nitric acid instead of hydrochloric acid, in order to shorten the washing, there being no chloride to remove.

The filtrates are strongly concentrated separately* in platinum, a drop or two of ammonia being added toward the end to the second one, and filtered successively through the same small filter into a flask of 150 to 200 c.m.³ capacity, the ammoniacal filtrate serving as wash-water for the first dish and containing enough ammoniacal salt to prevent precipitation of magnesium in the first filtrate when mixed with it. If manganese has been deposited upon the surface of the dish, it is removed by hydrochloric and a drop or two of sulphurous acids, which mixture is then passed hot through the filter. A re-precipitation by ammonia is then made, and the precipitate collected again on the filter and added to the main one, the filtrate passing into the flask containing the previous one. If much manganese is present, of course a second precipitation by ammonia of the small precipitate may be required. In these cases there is no difficulty in getting all the manganese into the filtrate.

Ignition of the Precipitate.

The combined precipitates of alumina, &c., are ignited moist, in the paper, unless considerable iron is present, when the main one is dried, removed as far as possible from the paper, and the latter ignited separately to prevent partial reduction of a portion of the iron, which cannot then be wholly re-oxidised by heating or by treatment with nitric acid (see p. 101).

Alumina, in the quantities ordinarily found, cannot be fully dehydrated by the full heat of the Bunsen burner; it must be blasted for five or ten minutes. If iron is present in large amount, this last operation must be conducted so as to insure free access of air to the crucible (p. 137).

Recovery of Silica and Possible Barium in the Alumina Precipitate.

The precipitate is dissolved by fusion with acid potassium sulphate, an operation which is accomplished without trouble in from two to four hours if the temperature is kept low and the acid salt has been properly made free from water and excess of acid. The melt is taken up with hot water and considerable dilute sulphuric acid, the residue collected, weighed, and corrected by hydrofluoric and sulphuric acids for silica, which, as said before, rarely amounts to 1 m.grm. in weight, and further examined for barium (see p. 137) by dissolving any remaining residue in hot strong sulphuric acid and diluting with cold water.†

Estimation of Iron in the Precipitate of Alumina, &c.

Without regard to the presence of Vanadium.— The filtrate obtained in the preceding paragraph is reduced, hot, by hydrogen sulphide, boiled to collect sulphur, and the platinum sulphide‡ resulting from the bisulphate

* *Bulletin of the United States Geological Survey*, No. 176.

† The fact must not be overlooked that certain of the rare earths may pass completely into the filtrate if the basic acetate method is followed. If then, later, on rendering the combined filtrates ammoniacal, an unexpectedly large precipitate appears; this should be carefully examined as to its nature. In an analysis of piedmontite from Maryland over 2 per cent of rare earths, including cerium and others not identified, were quantitatively separated in this way from iron, alumina, &c.

* If, instead of sodium acetate, ammonia alone has been used to precipitate alumina, &c., it has sometimes happened in the experience of others than the writer that on concentration of the first filtrate a pale straw-coloured precipitate appeared, which remained on the filter with the traces of alumina that may also separate, although it is slowly soluble in hot water. This is said to be some compound of platinum, and attention is called to it here for the guidance of others who may notice it and be unaware of its character.

† Some years ago, in a series of analyses of rocks from the Leucite Hills, in Wyoming, there was obtained at this stage, when it was customary to dissolve the melt in cold water preliminary to precipitation of titanium by boiling the neutralised sulphuric solution in presence of sulphur dioxide, a white, more or less flocculent residue amounting to 1 to 3 per cent of the rock, which was at first taken to be a mixture of tantalic and columbic acids. Eventually it was found to consist apparently of nothing but TiO_2 and P_2O_5, with perhaps a little ZrO_2. By repeated fusion with acid potassium sulphate and leaching with cold water, it could be gradually brought into solution. It was these rocks which furnished the most striking instance of the peculiar milky sulphate residues mentioned on p. 137 as derived from the ignited silica. Knop (*Zeit. für Kryst.*, 18[8]5, vol. x., p. 73) seems to have obtained a similar mixture in analysing minerals from the Kaiserstuhl, in Baden, but its nature was not ascertained, though suspected to be, if not silica, columbiferous titanic acid.

‡ It may be mentioned that the precipitation of platinum from a hot sulphate solution is far quicker and cleaner than from hydrochloric acid. Further, this platinum sulphide, when ignited in he

fusion, the hydrogen sulphide being allowed to pass for a short time after boiling. It is then filtered* hot into a flask attached to a carbonic acid apparatus and brought to boiling to expel hydrogen sulphide. When this is fully effected, the flask is cooled in water while the carbon dioxide still passes, and the solution is then titrated by potassium permanganate. The results are strictly accurate, with the limitations set forth in the paragraph below, when care is taken with the reduction by hydrogen sulphide. The method is altogether superior to that involving the use of zinc, since no foreign impurity affecting the result is introduced and the ever-present titanium is not affected, nor is vanadium reduced below the condition of V_2O_4, whereas nascent hydrogen converts it, in part at least, to V_2O_3. Titanium can be conveniently estimated by adding hydrogen peroxide to the titrated iron solution (see *prox.*).

Having regard to the presence of Vanadium. — If vanadium is present the value found for iron will be in error by the amount of permanganate required to oxidise V_2O_4 to V_2O_5. The amount of the correction will differ according as titration of the iron is made after reduction by hydrogen sulphide or by nascent hydrogen. If the former is used, as should always be the case, because of the ever present titanium, the vanadium is reduced by it to V_2O_4, which in its action on permanganate is equivalent to two molecules of FeO, while the reduction goes further with hydrogen. After the first transitory pink blush throughout the liquid, the slower-acting vanadium may require the addition of a drop or two more of permanganate before a comparatively permanent colouration appears.

When the amount of vanadium in the rock is known a correction can be applied on the assumption that practically all the vanadium is here collected, a point that needs further investigation. Various authors assert its precipitability with alumina and iron by ammonia and ammonium-acetate, though Carnot (*Comptes Rendus*, 1887, vol. civ., p. 1803; *Zeit. für Anal. Chem.*, 1893, vol. xxxii., p. 223), states that repeated precipitation by ammonia, ammonium carbonate, or ammonium sulphydrate, separates it from iron. The writer's experience with ores very rich in vanadium shows that precipitation along with iron and aluminum is only partial. Ridsdale (*Journ. Soc. Chem. Industry*, 1888, vol. vii., 73), has determined its precipitability with various metals, and gives numerous figures which show an approximation to 90 per cent thus thrown down under the conditions prevailing in analysis of iron slags, the remainder passing into the filtrates, and appearing in small part with the lime, and to a greater extent with the magnesium phosphate. For all practical purposes it is probably safe to assume that the small amounts of vanadium met with in rocks are wholly in the alumina precipitate.

If the amount of vanadium in the rock is not known, and great accuracy is necessary, caution requires the determination of the total iron to be made either in a separate portion or after re-precipitation from the above solution, as follows:—Fuse with sodium carbonate, extract with water, bring the insoluble residue into sulphuric solution, reduce, and titrate as above directed. But unless a certain precaution is here observed an error greater than that which it is designed to avoid will be committed. Contrary to general belief the aqueous extract from the sodium-carbonate fusion carries a small but appreciable fraction of a per cent of iron, as the writer has repeatedly found by actual test. This iron is thrown out with the alumina (and silica, if present), by the usual methods of neutralising the alkaline solution, and can be brought to light when the precipitate thus formed is treated with a fixed caustic alkali, or again fused with sodium carbonate, and leached with water, when it remains wholly or in part undissolved. Hence it is necessary to collect this iron, and add it to the main portion before titration.

Determination of the true Value for Ferric Iron.

Having in one way or another found the total iron in the rock, it remains to deduct an amount equivalent to the ferrous oxide the rock contains, and a further amount corresponding to the sulphides often present, in order to get what may pass for the true value for ferric iron. That this is often only an approximation appears from the difficulties due to the presence of vanadium, and the generally indeterminable effect of sulphides on the ferrous oxide determination. (See *prox.*).

(To be continued).

crucible in which the bisulphate fusion was made, should weigh, together with the crucible itself, what the latter weighed before the main silica precipitate was ignited in it; in other words, the weight of the platinum recovered by hydrogen sulphide should equal the loss in weight of the crucible due to attack by the bisulphate. In somewhat rare instances this will not be so, but the weight will be greater, showing a gain in platinum which may amount to a milligrm. Tests have shown that this is not due to retention of platinum by the main Al_2O_3, &c., precipitate; hence, it must come from platinum mechanically loosened from the dish during the drying and powdering of the silica preparatory to its collection on the filter, or to some insoluble compound of platinum formed during evaporation and drying of the silica. It may also be in part or wholly due to contamination from reduction of platinum during evaporation of the filtrate from the basic acetate separation. It will be remembered that from this filtrate a small amount of iron and alumina is recovered and added to the main precipitate. Hence it is always well in fine work to collect the sulphide and weigh the platinum in the original crucible, deducting any excess from the alumina, or else to get rid of the platinum by hydrogen sulphide before proceeding to the precipitation of alumina, &c. (see p. 138).

* Filtration is not necessary if only precipitated sulphur and no sulphides are in suspension, since this is without reducing action on cold permanganate solution, as Wells and Mitchell, and others before them, have pointed out. The above authors used this method of reducing ferric iron in titanic iron ores (*Journ. Am. Chem. Soc.*, 1895, vol. xvii., p. 78; also Chemical News, 1856, vol. lxxiii., p. 123).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, March 22nd, 1901.

Prof. S. P. Thompson, President in the Chair.

By invitation of Professors Callendar and Ramsay, this meeting was held in University College.

A paper "*On the Expansion of Silica*" was read by Prof. Callendar.

The extreme smallness of the thermal expansion of silica (fused quartz) renders the determination of its coefficient of expansion more difficult than is the case with many substances. The author has made experiments upon a rod of pure silica 40 c.m. long and 1 m.m. diameter. This rod was enclosed in a platinum tube about 3 m.m. diameter, which could be raised to various temperatures by the passage of a suitable electric current. Both the rod and the tube were firmly fixed at one end, and the positions of the other ends were accurately observed by a micrometer microscope reading to a thousandth of a m.m. The expansion of the tube, in conjunction with a knowledge of its coefficient of expansion, served as a means of determining the temperature of the tube, and therefore of the rod. The increase in length, the original length, and the range of temperature of the silica being known, the coefficient of expansion can be at once calculated. In some previous experiments the author has investigated the distribution of temperature along a heated platinum rod subjected to cooling at the ends. These experiments prove that the error due to end effect, in the case of the silica rod, can be neglected.

The expansion of silica up to 1000° C. is regular, and is about one-seventeenth that of platinum. Between 1000° C. and 1400° C. silica expands more quickly than below 1000° C., and if left at any temperature for a considerable time continues to slowly increase in length. If a curve be plotted, having temperatures as abscissæ and increases in

length as ordinates, a straight line will represent the expansion of silica up to 1000° C. Above 1000° C. the curve bends upwards, and upon cooling it returns along a path above the ascending curve, so that the final length of the bar is greater than the original length when the lower temperature is reached. The determination of the coefficient of expansion at these high temperatures was made by means of a variable zero; that is, by using for the length of the rod that obtained by suddenly cooling from the higher to the lower temperature. At 1400° C., the properties of silica alter, and the expansion is replaced by a contraction. On cooling from above 1400° C. to ordinary temperatures, there is first an expansion and then a contraction. This property was illustrated by Prof. Callendar, the small changes in length of the rod being magnified by a lever and shown upon a screen by an optical arrangement. The critical point at which contraction occurs on heating has been found by Le Chatelier at about 800° C. His experiments were made by a differential method, using porcelain as a standard substance. As the expansion of porcelain is uncertain, the author thinks it probable that the effect noticed may be due to irregularities in the expansion of porcelain rather than in that of silica.

Mr. BOYS expressed his interest in the experiments and asked if the small coefficient of expansion of slate had ever been measured. The small expansion of silica would make it a useful suspension for pendulums, on account of the small compensation necessary. Its perfect elastic properties might be made use of in hair springs for chronometers.

Prof. THRELFALL said that he had tried to measure the expansion of silica between 0° C. and 70° C. by weighing rods in distilled water, but the method was not accurate. He had made experiments similar in principle to the authors, using temperatures from 0° C. to 100° C. The devitrification of silica is troublesome, and he thought that the rate of devitrification in presence of air increased with the temperature.

Dr. DONNAN thought that the irregularities in the expansion of silica pointed to a complex composition.

Mr. PORTER (Eton) asked if the effect of fused quartz on polarised light had been investigated, and if this effect altered after heating to 1400° C.

Mr. BOYS said quartz rods formed by fusion depolarised light.

The CHAIRMAN said that he had noticed the effect spoken of by Mr. Boys, due to strain, but he had been unable to detect any rotatory power.

Prof. CALLENDAR, in reply to Mr. Lupton, said that the expansion of quartz crystals was much larger than that of fused silica.

The Spectroscopic Apparatus of University College was then exhibited by Dr. BALY.

The Society then adjourned until April 26th, 1901.

Constitution of Gentianose.—Em. Bourquelot and H. Hérissey.—Gentianose is a hexotriose, to which the formula $C_{18}H_{32}O_{16}$ can be given. This formula demands a molecular weight of 504, and the authors have found by Raoult's method 494·3.—*Comptes Rendus*, cxxxii., No. 9.

Action of Cyanide of Potassium on the Fatty Aldehydes.—L. Kohn.—Cyanide of potassium reacts very briskly on formic aldehyde, to such an extent, in fact, that if it is not kept cool the whole begins to boil, and the mixture rapidly becomes black. By keeping it cool we obtain a mixture of glycolate of potassium and hexamethylenetetramine,—

$$10CH_2O + 4CNK + 2H_2O = (CH_2)_6N_4 + 4CH_2OH—CO_2K.$$

By operating with a solution of an equimolecular mixture of cyanide of potassium and chloride of calcium we obtain a deposit of carbonate with crystals of glycolate of calcium.—*Mon. f. Chim.*, vol. xx., p. 903.

NOTICES OF BOOKS.

A Manual of Elementary Science; A Course of Work in Physics, Chemistry, and Astronomy for the Queen's Scholarship Candidates. By R. A. GREGORY, F.R.A.S., Professor of Astronomy, Queen's College, London, and A. T. SIMMONS, B.Sc. (Lond.), Associate of the Royal College of Science, London. London: Macmillan and Co., Limited. New York: The Macmillan Company. 1901.

THIS book is an attempt to give a small amount of knowledge upon a vast number of subjects to meet the requirements of students of elementary science with the view of presenting themselves in that subject at the "Queen's Scholarship examination." The arrangement of the subject matter is good, and much pains have been taken to encourage the student to construct apparatus and make experiments to demonstrate the principles involved. Unfortunately, as is nearly always the case where much has to be condensed into a very small space, many of the descriptions are too meagre to be of any value to the student, and in some cases the authors attempt to describe apparatus of which they apparently have no knowledge. An instance of this is to be seen on page 103 in the drawing and description of a Sprengel air-pump. We should not have thought it possible for such a totally erroneous and absurd description of a common piece of apparatus to appear in an educational book in the year 1901! Similar carelessness is shown in the description of how to make a thermometer on page 112; the student is told to "procure an empty thermometer tube with a bulb at one end. (If a blowpipe is available a bulb can easily be blown upon one end by melting the glass in the flame, and blowing down the open end while the other end is molten)."

Such a description, and what follows as to filling such a tube with mercury are utterly valueless, and would only mean failure and disappointment to any student who attempted to follow it!

There are a large number of illustrations, both old and new, some of which leave much to be desired. By far the best part of the book is that devoted to astronomy; here both the illustrations and the descriptions are exceedingly good, and partly atone for the shortcomings of the preceding chapters. There is a good index, and the price is moderate.

Modern Chemistry, Theoretical and Systematic. In two volumes. By WILLIAM RAMSAY, D.Sc. London: J. M. Dent and Co. 1900. Pp. 330.

THOUGH called "Modern Chemistry" these two volumes have in their title-pages and frontispieces a decidedly "old" appearance; the portraits of the Hon. Robert Boyle and John Dalton remind us of the good old days when practically all chemical science could be carried in one head.

The author first deals with the "phlogiston" theory which was conceived by Stahl early in the eighteenth century. In this connection we note that he suggests the word "burnableness" as the translation of "phlogiston." Surely "inflammability" would be equally good, and less clumsy. He then rapidly passes over the discovery of gases, Dalton's laws, Avogadro's hypothesis, atomic and molecular weights, &c., and in Chapter IV. he considers the classification, periodicity, and valency of the elements.

The second volume is on systematic, or what is more commonly called practical chemistry, though while describing the preparation and properties of the salts and compounds met with in inorganic chemistry it does not appear to deal with any system of chemical analysis.

Some of the ideas introduced by the author are of an original kind, but on the whole we think these two volumes are more suitable for thoroughly grounded chemists than for students.

CORRESPONDENCE.

AMERICAN *v.* ENGLISH SPELLING.

To the Editor of the Chemical News.

Sir,—I entirely agree with your reviewer in his remarks anent American spelling, and cannot see that Dr. Carrington Bolton has made out any case for his objection to them. The way in which Americans spell their words is entirely a matter for themselves: if they prefer "sulfur," as in French, by all means let them have it; but I must emphatically deny that it is English.

English spelling is to a great extent bound up with the history of our nation, but in America they have no history and but little veneration.

It is really absurd to describe *English* spelling as "erroneous" and to sneer at it as "archaic" simply because four American professors appointed as a committee in 1888 decided to alter it—in America.

Dr. Carrington Bolton asks for peace, but we are bound to defend our language from the entirely unnecessary innovations of American spelling "reformers." Does not Dr. Carrington Bolton well know that the addition of an "e" to the word "oxid" changes the sound of the "i" from short to long, "oxīd" to "oxide"? The same applies to "chlorīn," "bromīn," &c.

There is another point to which I should like, Sir, to call your attention, and that is the mischievous American use of the word "billion," which word has recently been brought into prominent notice in connection with the "Steel Trust." Now a "billion" is a million million, or a million to the second power $1{,}000{,}000^2$, that is 1,000,000,000,000; in America the word "billion" is used to express one thousand millions, 1,000,000,000, and is the same as the French milliard.—I am, &c.,

An English Chemist.

SEPARATION OF FERRIC CHLORIDE FROM OTHER METALLIC CHLORIDES BY ETHER.

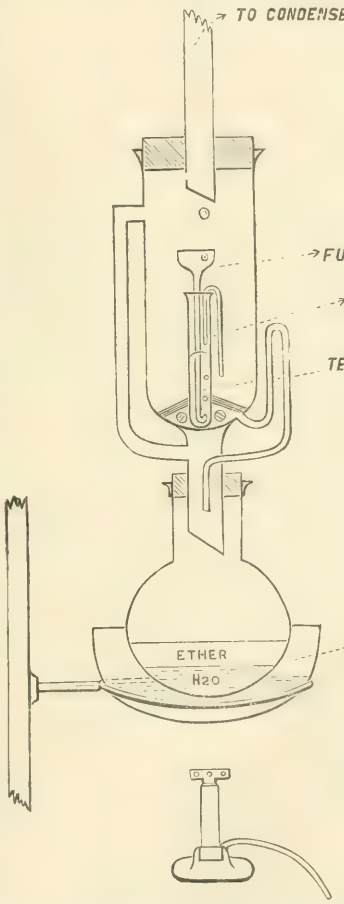
To the Editor of the Chemical News.

Sir,—It may be interesting to Mr. Speller and other readers to give the details of a method used for estimating nickel in steel in a laboratory with which I was connected some time ago. I am indebted to the late Mr. Thomas Hilditch for the details of the method.

1 grm. of the steel was dissolved in HCl, oxidised with HNO_3, and taken to dryness. It was re-dissolved in HCl, and evaporated to a thick syrup, in a small ½-oz. beaker, but not low enough to turn basic; it was now transferred to a small test-tube about 3" long and ⅝" diameter, the beaker being washed into the tube with the *minimum* amount of dilute HCl, made from HCl (1·2) 1 part, and water 1 part. Total bulk should not now exceed 25 or 30 c.c.

The tube was put into a Soxhlet's fat extracting apparatus, and a small funnel put into the tube to cause the ether to circulate through the test liquid. (See diagram). The apparatus is started, and can now proceed without further attention. At the end of one or two hours the ethereal extract will be quite colourless, showing that the iron has been taken out, and a green solution will be present in the test-tube. The ether is decanted off as much as possible, and the solution transferred to a beaker, and boiled to expel all the remaining ether, acidified with a few drops of HCl, and, in the absence of chromium, a slight excess of ammonia added; the traces of iron, if any, remaining behind, are precipitated. These are filtered off, and the clear blue solution titrated with a standard solution of potassic cyanide, using silver iodide as an indicator. The AgI was precipitated in the solution by adding a measured amount of silver nitrate and excess of KI to produce a slight turbidity. The same amount of $AgNO_3$ of course being added to the solution of nickel used in standardising the KCN, and running in KCN until solution is faintly opalescent in each case

The Soxhleting operation can be much shortened by previously giving the solution of the steel "a wash" with ether by pouring ether down the small funnel.



The water in the bottom of the flask washes most of the ferric chloride out of the ether as well as heating the ether more moderately.

If chromium is present as well the nickel is separated after "Soxhleting" by means of bromine and NaHO, the washed precipitate re-dissolved in HCl, boiled, and ammonia added as before.—I am, &c.,

H. Procter Smith.

Harrington Road, Workington.
March 19, 1901.

RAPID ESTIMATION OF PHOSPHORUS IN STEEL.

To the Editor of the Chemical News.

Sir,—As regards the rapid estimation of phosphorus in steel, I have for a considerable period employed the following method, and have found it to yield very satisfactory results, both as regards accuracy and rapidity :—

To 3 grms. of the sample, contained in a 12-oz. assay flask, add 20 c.c. 16E HNO_3 and 20 c.c. of water. (Steels of practically the same chemical composition behave very differently with this acid mixture, some remaining passive in the cold, while others are immediately attacked).

When the sample is dissolved (heat is applied to accelerate the action), the solution is heated to boiling, and while at this temperature a strong solution of $KMnO_4$ added until the colour of the liquid remains a permanent pink and MnO_2 is precipitated, and the boiling continued for two to three minutes. 10 to 12 c.c. of 10E HCl are then added, the solution boiled for two to three minutes, and the clear solution cooled. To the cold solution 20E NH_4HO added (with brisk agitation of the containing vessel) until the whole of the iron is precipitated (generally a semi-solid mass is obtained), and a slight excess, as judged by smell, of NH_4HO is present. 16E HNO_3 is now added (in small quantities at a time, and with brisk agitation of the containing vessel), until a perfectly clear solution is obtained (usually 10 to 12 c.c. 16E HNO_3 are required). To the solution now add 10 c.c. of ammonium molybdate solution (100 grms. ammonium molybdate per litre of water), then 3 to 4 c.c. 16E HNO_3, the solution briskly shaken, and allowed to stand in a warm place for some time. The resulting ammonium phosphomolybdate precipitate collected on an English filter-paper, washed a few times with a 1 per cent solution of nitric acid, dried at about 110° C., and weighed.

With basic and other phosphoric pig-irons containing up to 1·5 to 2 per cent of silicon (working on 0·5 grm. of the sample, filtering before oxidising with $KMnO_4$, and using 20 c.c. of the ammonium molybdate solution and 6 to 8 c.c. 16E HNO_3 for the precipitation of the phosphorus), the above process gives higher results than those yielded by the ordinary methods. This may be due to the formation, in the ordinary methods of analysis, of an insoluble phosphate. On the other hand, the high results obtained by the rapid method may be due to the phosphorus precipitate carrying down along with it silica. What is the real cause of the discrepancies, want of time has prevented me investigating. I am, however, satisfied that it is not due to arsenic, as this element is not present in anything like sufficient quantities to affect the results to such an extent.—I am, &c.,

J. Jas. Morgan, F.I.C.

Wednesbury, March 18, 1901.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxii., No. 9, March 4, 1901.

Method of Estimation of Sulphides, Sulphohydrates, Polysulphides, and Hyposulphites coexisting in Solution, especially in Sulphurous Mineral Waters.—Armand Gautier.—The author describes a method of analysis by which sulphides, sulphohydrates, and hyposulphites can be separately estimated in the same water. This method was applied to two waters; the first being prepared by heating finely-powdered granite with its own weight of water to 280°, and th second being the water of Labassère (Ariège).

Preparation and Properties of Sulphammonium.—Henri Moissan.—By the action of sulphur on liquefied ammonia, the author obtains a new compound—sulphammonium. This substance has a dark red colour, and it is completely dissociable at ordinary temperature and pressure. It has the property of giving up its sulphur easily in the cold to a great number of simple and compound bodies.

Germination in Distilled Water.—P. P. Dehérain and M. Demoussy.—The authors' experiments show—(1) That germinating seeds form their roots and start their evolution in water absolutely free from chalk; (2) that the development of the root during germination stops when it is placed in distilled water containing even minute traces of copper; (3) that living seeds can be used to detect infinitesimal quantities of a metal such as copper, which any ordinary chemical reaction would fail to detect.

A New Method of Determining the Atomic Weight of Uranium.—J. Aloy.—From a knowledge of the nitrogen and uranium contained in the same weight of nitrate, the atomic weight of uranium can be determined with respect to that of nitrogen. Taking the latter as 14·04, the author finds that the atomic weight of uranium differs very slightly from 239·4.

Thermal Examination of the Ammoniacal Chlorides of Aluminium.—L. Baud.—In a former paper, the author announces the fact that anhydrous aluminium chloride will combine with ammonia gas in the proportions—$Al_2Cl_6.2NH_3$, $Al_2Cl_6.10NH_3$, $Al_2Cl_6.12NH_3$, $Al_2Cl_6.18NH_3$. All these substances are decomposed by water, and, by using M. Berthelot's calorimeter and system of correction, the author examines these compounds thermometrically, finding their heats of solution and deducing the heats of fixation of a molecule of ammonia. He reserves an examination of the compound $Al_2Cl_6.18NH_3$ for a future research, as it presents interesting peculiarities.

A New Cobalt Silicide.—Paul Lebeau.—The method of preparation of metallic silicides by the action of a metal on copper silicide allowed of the discovery of a new compound of silicon and cobalt corresponding to the formula SiCo. This substance is comparable in its composition and its properties with iron silicide, SiFe. Cobalt silicide is remarkable for the manner in which it resists oxidising agents, and for the very slight action of acids (except hydrochloric acid) upon it.

Mixed Organo-magnesium Compounds.—V. Grignard.—The organo-magnesium halogen compounds present the following properties :—(1) They are solid and not spontaneously inflammable in air; (2) they are formed without liberation of magnesium bromide or iodide; (3) by union with the aldehydes or the ketones, they give compounds which contain all the halogen employed, and which, by the action of water, are decomposed with formation of a secondary or tertiary alcohol without evolution of any gas.

An Isomer of Anethol and its Constitution.—MM. Béhal and Tiffeneau.—When methyl-magnesium iodide acts on anisate of methyl, parapseudopropenylanisol is formed; the reaction being represented by the equation—

$$CH_3{-}O{-}C_6H_4{-}CO_2C_2H_5 + 2I{-}Mg{-}CH_3 =$$
$$= CH_3{-}O{-}C_6H_4{-}C(CH_3){=}CH_2 + MgO + MgI_2 + C_2H_5OH.$$

The propenylanisol thus formed is condensed and doubles its molecule. The substance is then in the form of crystals fusing at 32°; it boils at 222° at ordinary pressure, and possesses a mixed odour of anethol and estragol.

Phenylhydrazones of *d*-Glucose and their Multirotation.—L. J. Simon and H. Bénard.—A preliminary examination of the multirotation of the hydrazones of Fischer and Skraup shows—(1) The hydrazone of Fischer possesses multirotation; (2) the final rotations are the same for the two isomers; (3) the initial rotation, which, for Skraup's

hydrazone is, in absolute value, inferior to the limit, in Fischer's hydrazone is, on the contrary, superior to the limit; (4) the time employed for the two hydrazones to take their rotation limit is of the same order of magnitude.

General Method of Synthesis of Naphthenes.—Paul Sabatier and J. B. Senderens.—The activity of nickel for regularly inducing hydrogenation of benzene is a property peculiar to this metal. The same property is exercised with regard to hydrocarbons homologous to benzene. All the carbides used by the authors were directly hydrogenated towards 170° or 200° in presence of reduced nickel; in all cases the corresponding hexahydride being formed. The above forms a general and very simple method for effecting the synthesis of the naphthenes or substituted cyclohexanes.

Specific Heat and Heat of Fusion of Ethylenic Glycol.—M. de Forcrand.—The author's experiments show that the probable specific heat of solid glycol is 0·265 for 1 grm. towards its point of fusion. As to the latent heat of fusion, it is −2·66 calories for 1 molecule, having been deduced from analogy. The latent heat of vaporisation has been determined by M. Longuinine, and found to be −12·06 cals. for the molecule at 197°.

MISCELLANEOUS.

Bryan Corcoran Limited.—This firm has acquired the name, goodwill, and business of Bryan Corcoran, Witt, and Co. The businesses are now merged in one, and will be carried on under the title of Bryan Corcoran Limited. The business was originally founded in Mark Lane by Bryan Corcoran in 1780. He was succeeded by his son, the late Bryan Corcoran, in 1833. The Managing Director, Mr. Bryan Corcoran, is the only son of the latter, and grandson of the founder. The business was carried on by him for twenty-five years in his own name, and was in 1896 formed into this company, which now unites all interests.

A New General Reaction for Albumenoid Materials.—A. P. Lidof.—If we gently heat a solution of any proteïc material with $AgNO_3$ and a slight excess of KOH, we observe almost immediately a brownish colouration, which increases in intensity until the liquid finally assumes a very deep tint. In certain cases the liquid, after a longer or shorter time, forms a silver mirror on the sides of the vessel; in most cases, however, it does not change in appearance, even after a very long time. The intensity of the colouration is the greater as the precipitate of Ag_2O produced by the KOH is less, which indicates that the Ag_2O gradually becomes reduced to the state of metallic Ag, which remains dissolved. The author has examined eighteen different albumenoid materials, such as caseine, legumine, globuline, vitelline, colloidine, gelatin, hemo globin, &c. In most cases the reaction takes place in the same manner; only with mucine, besides the colouration a black precipitate is formed, which increases with time, while the liquid becomes colourless. As mucine contains a relatively large amount of sulphur, sulphide of silver is no doubt formed. Fibroïne from silk and some other albumenoid bodies show this peculiarity, that the silver in solution is gradually deposited, forming a mirror; this also occurs with myosine, caseine, and spongine, but with this latter the silver separates in the form of a yellow modification. It should be mentioned that the presence of ammonia prevents the formation of dissolved silver. The influence of light is important; with gelatin solution kept in the dark the colouration is not produced; with albumin the thick solution formed by the $AgNO_3$ becomes more fluid and coloured in the light, while it does not change in the dark. The author thinks that in gelatin-bromide photographic plates silver in solution is formed. Silver solutions thus prepared will dye animal or vegetable fibres without the use of any mordant; the tint produced is practically that which exposure to light has given to the liquid. As an insignificant quantity of silver is able to produce an intense colouration, the process may possibly become of practical value.—*Journ. Soc. Phys. Chim. R.*, vol. xxxi., p. 781.

Hydroxylammoniated Compounds of Platinum.—R. Uhlenbuth.—The author describes the hydrate of platoso-dihydroxylammonium, $Pt{<}^{(NH_2OH)_2OH}_{(NH_2OH)_2OH}$ (corresponding to Reiset's first base), and its salts. To a dilute solution (1·5 per cent) of $PtCl_4$ he adds a solution of pure hydroxylamine. A brisk disengagement of nitrogen takes place; on boiling, the solution becomes decolourised, and on cooling deposits the base in white crystals insoluble in water, alcohol, and ether, but soluble in the mineral acids and acetic acid. It is formed according to the following equation:—

$$PtCl_6H_2 + 12NH_2OH = Pt(NH_2OH)_4(OH)_2 + 6NH_2OH.HCl + N_2;$$

this body detonates at 173°. The sulphate, $Pt(NH_2OH.NH_2OH)_2SO_4 + H_2O$, is deposited on cooling in large triclinic crystals slightly soluble in water. The chloride, $Pt(NH_2OH.NH_2OH)_2Cl_2$, is soluble in water, and crystallises in flattened needles. The nitrate crystallises in brilliant colourless needles. Concentration of the mother-liquors of the chloride on the water-bath gives long radial needles, forming a golden-yellow solution in alcohol, and even in ether. The solution of this body hardly becomes cloudy on the addition of NO_3Ag. Its composition is $Pt(NH_2OH)_2Cl_2$ (corresponding to Reiset's second base). We can obtain a salt of the same composition, but in blue crystals by the addition of $PtCl_4$ to the solution of the chloride, $Pt(NH_2OH)_4Cl_2$. The blue salt only gives up half its chlorine to NO_3Ag.—*Lieb. Ann.*, vol cccxi., p. 124.

MEETINGS FOR THE WEEK.

Monday, April 1st.—Society of Chemical Industry, 8. "The Effect on the Marsh Test of some Commercial Products containing Selenium and Tellurium," by A. E. Berry. "A New System for the Manufacture of Borax and Nitrates," by Dr. W. Newton. "Basic Superphosphate—its Preparation and Use as a Manure," by J. Hughes. "The Preparation of Pure Cineol from Eucalyptus Oil by means of the Arsenate," by Watson Smith. "Action of Caustic Potash and Soda on Stannous Sulphide," by Dr. F. Mollwo Perkin.

Wednesday, 3rd.—Society of Public Analysts, 8. "The Maumené Test for Oils," by C. A. Mitchell, B.A., F.I.C. "Some Arsenic Estimations relating to Malt Kilns," by T. Fairley, F.I.C. "The Aeration Test for Effluents," by S. Rideal, D.Sc., F.I.C.

ST. PAUL'S SCHOOL.—An Examination will be held at St. Paul's School, West Kensington, on Tuesday, April 16th, and following days, for filling up about Eight Vacancies on the Foundation.—Full particulars can be obtained on application to the Bursar.

ACETONE.
JOHS. OSWALDOWSKI,
ALTONA, near HAMBURG.

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THE CHEMICAL NEWS.

VOL. LXXXIII., No. 2158

THE MINERAL CONSTITUENTS OF DUST AND SOOT FROM VARIOUS SOURCES.*

By W. N. HARTLEY, F.R.S., Royal College of Science, Dublin, and HUGH RAMAGE, A.R.C.Sc.I., St. John's College, Cambridge.

BARON NORDENSKJÖLD has described three different kinds of dust which were collected by him (*Comptes Rendus*, vol. lxxviii., 236). Of two of these, one consisted of diatomaceæ and another of a siliceous and apparently felspathic sand; both were found on ice in the Arctic regions. The third variety was quite different and appeared to be of cosmic origin. He observed that some sand collected at the end of a five or six days continuous fall was mingled with a large quantity of sooty-looking particles, consisting of a material rich in carbon. It appeared to be similar to the dust which fell, with a shower of meteorites, at Hessle, near Upsala, in the beginning of the year 1869. As in this particular instance it might be supposed that the railways and houses of Stockholm had contributed some of this matter to the atmosphere, and that the snow had carried it down, he requested his brother, who then resided in a desert district of Finland, to give his attention to the subject, with the result that he collected a similar powder. The snow gathered in the latitude of 80° N. in an expedition to Spitzbergen, and that collected from floating ice in the Arctic regions, and on the glaciers of Greenland, leaves, after it has melted, a greyish residue, which consists largely of diatomaceæ, but mixed with these organisms there were also particles of a carbonaceous dust of considerable size, which on analysis were found to contain metallic iron, cobalt, and nickel, also silicon, carbon, and phosphorus. The origin of this mineral matter was at first doubtful. Two of its constituents, cobalt and nickel, were believed to be of very uncommon occurrence in terrestrial matter, while, on the other hand, they are elements invariably associated with the metallic iron of meteorites, the nickel being more particularly in large proportion. If we suppose that this dust is discharged from the mouth of a distant volcano, or that it may be sand carried up by a whirlwind, we have yet to explain the peculiarities in its composition which render it similar to that of meteorites.

Nordenskjöld arrived at the conclusion that it was meteoric matter which had descended upon the earth in a shower similar to that which occurred near Upsala. By the facts which he had collected it appears to have been proved that cosmic dust is falling imperceptibly and continually. It seems that this view is either generally not accepted, or that the facts are not commonly known.

Very little is really known about the composition of atmospheric dust, notwithstanding that searching investigations were made by Pasteur and Angus Smith, aided by the microscope, and later by Liveing and Dewar by the aid of the spectroscope.

Professor O'Reilly, M.R.I.A., supplied us with small quantities of a material concerning the nature of which he was desirous of obtaining information. On inspection it appeared to be of an unusual character for mere town dust, and accordingly we submitted it to a spectrographic analysis, and determined the principal metallic elements which enter into its composition. The following specimens in particular have been examined with care:—

I. Solid matter which fell in or with hail in a hail-storm on Wednesday, April 14th, 1897, and was collected by Professor O'Reilly at a window facing the large open space of Stephen's Green, at the Royal College of Science, Dublin. It contained iron, sodium, lead, copper, silver, calcium, potassium, nickel, manganese a trace; gallium and cobalt gave doubtful indications.

II. Solid matter from hail and sleet collected by Professor O'Reilly from a window-sill of the Royal College of Science, Dublin, during a very heavy shower, from 2.30 till 3 o'clock, in the afternoon of March 28th, 1896.

Total weight of the dust 0·1018 grm., of which 0·08 grm. was burnt in the oxyhydrogen flame. The colour of the dust was steel-grey, and it was magnetic. It contained iron, copper, and sodium, lead, calcium, potassium, manganese, nickel, silver, thallium a trace, gallium, and rubidium a trace, doubtful.

III. Pumice from Krakatoa eruption, 1883; from Professor O'Reilly. By decomposing the silicate with ammonium fluoride and sulphuric acid, and precipitating the solution with ammonia, the following bases were separated:—Iron, copper, silver, sodium, nickel, potassium, rubidium, manganese, gallium, and indium a trace (*Trans. Chem. Soc.*, 1901, vol. lxxix., p. 61).

The salt separated by filtration and evaporation of the filtrate contained sodium, potassium, calcium, copper, silver, strontium, nickel a trace, rubidium, and manganese. With the very notable exceptions of strontium, nickel, and cobalt we have found these constituents in ninety-seven irons, ores, and associated minerals (nickel was found in twenty-three, *Trans. Chem. Soc.*, 1897, vol. lxxi., p. 533). On the other hand, in the examination of six meteoric irons, we have found the same elements invariably associated with nickel and cobalt, the last-named being always in much smaller proportion than the nickel (*Sci. Proc. Dublin Soc.*, New Series, vol. viii.). Had it been possible to operate on larger quantities, we quite expect that cobalt would have been found in this dust, but the small amount of 8 centigrms. is insufficient for such a purpose, even in the case of most meteoric irons. It is rather a striking fact that in the dust No. 2 there is a trace of thallium. This is rather suggestive of its being probably pyrites flue dust, a substance which might occur in hail or rain in a neighbourhood where sulphuric acid is manufactured. It might possibly come from an admixture of soot yielded by a coal containing thalliferous pyrites.

There are three vitriol works within two or three miles of the College, but after taking all the facts into consideration, we are not able to admit this source as a probable means of contamination, for, as will be seen from analyses to be presented, there is one notable constituent we have found in flue dust which is absent from the samples I. and II., namely indium.

In 1897, in order to push this inquiry somewhat further, dust was collected in porcelain dishes placed upon a grass plot in the garden of a residence just on the outskirts of Dublin[1] during a period from the 15th November to the 15th December. A considerable fall of a carbonaceous-looking matter occurred on the 16th and 17th of November; some of the particles were 2 or 3 m.m. in diameter, and had a steel grey appearance rather like hard coke or graphite. These particles all sank in the rain-water which collected on the 17th or 18th, while a large number of sooty particles floated; as the dish became over-filled, the sooty matter was automatically washed away, and only the heavier particles remained. The contents of the dishes were poured into glass cylinders, and after the heavier particles had been deposited the water was removed by decantation.

Subsequently it became interesting to ascertain what substances are to be found in ordinary soot and flue dust—dust from volcanic eruptions, &c. We have tabulated the results and arranged together those substances which we know to have the same origin.

The specimens of soot required no preliminary treatment before being burnt, and the analysis of each is given

* A Paper read before the Royal Society, February 21, 1901.

[1] At the back of my house and remote from any factory chimneys.—W.N.H.

THE COMPOSITION OF DUST FROM VARIOUS SOURCES.

	Sodium.	Potassium.	Rubidium	Cæsium.	Copper.	Silver.	Magnesium.	Calcium.	Strontium.	Aluminium.	Gallium.	Indium.	Thallium.	Iron.	Nickel.	Cobalt.	Manganese.	Chromium.	Lead.	Zinc.	Cadmium.	Tin.
Dust from sleet, fell March 28th, 1896 ..	Na	K	Rb?	..	Cu	Ag	..	Ca	..	..	Ga	..	*Tl*	Fe	Ni	..	Mn	..	Pb			
Dust from hail, fell April 14th, 1897	Na	K	..	..	Cu	Ag	..	Ca	..	..	Ga?	..	..	Fe	Ni	..	*Mn*	..	Pb			
Dust from the clouds, fell November 16th and 17th, 1897	Na	K	..	..	Cu	Ag	..	Ca	..	..	Ga	..	*Tl*	Fe	Ni	..	Mn	*Cr*	Pb			
Dust from rain, November 13 to 15th, 1897	Na	K	..	..	Cu	Ag	..	Ca	*Sr*	..	*Ga*	..	*Tl*	Fe	Ni	..	*Mn*	..	Pb			
Volcanic dust from New Zealand—																						
(1). Te Ariki	Na	K	Rb	..	Cu	*Ag*	MgO	Ca	Sr	..	*Ga*	..	..	Fe	*Ni*	..	Mn	..	Pb			
(2) Tarranga..	Na	K	Rb	..	Cu	*Ag*	MgO	Ca	Sr	..	*Ga*	..	..	Fe	*Ni*	..	Mn	..	Pb			
(3). Te Hape-o-Toroa	Na	K	Rb	..	Cu	*Ag*	MgO	Ca	Sr	..	*Ga*	..	..	Fe	*Ni*	..	Mn	..	Pb			
Pumice from Krakatoa	Na	K	Rb	..	Cu	Ag	..	Ca	Sr	..	Ga	*In*	..	Fe	*Ni*	..	Mn	..	Pb			
Lead chloride from crater of Vesuvius ..	Na	K	Rb	..	Cu	..	..	..	..	..	..	..	Tl	Fe	..	..	..	..	Pb			
Soot from chimneys—																						
(1). A bedroom chimney	Na_9	K_4	*Rb?*	..	Cu_2	..	..	Ca_7	Sr_1	..	Ga_1	..	Tl_1	Fe_8	Ni_1	..	Mn_1	..	Pb_4			
(2) A kitchen chimney..	Na_3	..	..	..	..	..	..	Ca_3	..	..	..	..	..	Fe_2								
(3). A laundry chimney	Na_9	K_4	*Rb?*	..	Cu_4	Ag_1	..	Ca_7	Sr_1	..	Ga_2	..	Tl_2	Fe_9	Ni_3	..	Mn_3	Cr_1	Pb_5			
(4). Assay laboratory fusion furnace ..	Na_9	K_8	*Rb?*	..	Cu_4	Ag_4	..	Ca_2	..	..	Ga_3	..	Tl_3	Fe_7	Ni_3	..	Mn_1	..	Pb_9			
(5). Assay laboratory gas muffle.. ..	Na_7	K_3	..	..	Cu_3	Ag_2	..	Ca_3	..	..	*Ga?*	..	Tl_1	Fe_7	..	..	Mn_1	..	Pb_8			
(6). Heating apparatus furnace	Na_9	K_4	*Rb?*	..	Cu_3	..	..	Ca_9	Sr_2	..	*Ga?*	..	Tl_1	Fe_9	Ni_1	..	Mn_6	..	Pb_3			
Flue dust*—																						
(1). Gasworks, Crewe	Na	K	*Rb*	..	Cu	Ag	..	Ca	Sr	..	Ga	In	..	Fe	Ni	..	Mn	..	Pb			
(2) Boyd's Chemical Works, Dublin..	Na	K	..	..	Cu	Ag	..	Ca	..	..	..	In	Tl	Fe	..	..	..	..	Pb			
(3). Nicholson's Copper Works, Leeds, 0·5 grm..	Na	K	Rb	..	Cu	Ag	..	Ca	..	..	Ga	In	Tl	Fe	..	..	..	..	Pb			
Do. do. 20 grms.†	Na	K	Rb	*Cs*	Cu	Ag	..	Ca	Sr	Al	Ga	In	Tl	Fe	Ni	*Co*	Mn	Cr	Pb	Zn	Cd	Sn
(4). Ferro-manganese furnace, Pittsburg, U.S.A.	Na	K	Rb	..	Cu	..	..	Ca	..	..	..	..	Tl	Fe	Ni	..	Mn	..	Pb			
(5) Ferro-manganese furnace	Na	K	Rb	*Cs*	Cu	Ag	..	Ca	..	..	Ga	*In*	Tl	Fe	..	..	Mn	..	Pb			
(6). Cleveland iron furnace, Samuelson, Middlesbrough	Na	K	Rb	..	*Cu*	*Ag*	..	Ca	..	..	*Ga*	..	*Tl*	Fe	*Ni*	..	Mn	..	Pb			
(7). Cleveland iron furnace	Na	K	Rb	..	*Cu*	*Ag*	..	Ca	..	..	*Ga*	*In*	*Tl*	Fe	*Ni*	..	Mn	..	Pb			
(8) "Basic iron" furnace	Na	K	Rb	*Cs*	*Cu*	*Ag*	..	Ca	Sr	..	*Ga*	*In*	*Tl*	Fe	*Ni*	..	Mn	..	Pb			
(9). South Wales iron furnace	Na	K	Rb	..	*Cu*	*Ag*	..	Ca	..	..	*Ga*	*In*	..	Fe	..	..	..	..	Pb			
Examples of well-known Meteorites.																						
Meteoric stone, Alfianello	Na	K	..	..	Cu	Ag	MgO	Ca	..	..	*Ga*	..	..	Fe	Ni	..	Mn	Cr	Pb			
Meteoric stone, Pultush	Na	K	..	..	Cu	Ag	MgO	Ca	..	..	..	..	..	Fe	Ni	..	Mn	Cr	Pb			
Meteoric stone, Mocs	Na	K	..	..	Cu	Ag	MgO	Ca	*Sr*	..	..	..	..	Fe	Ni	..	Mn	Cr	Pb			
Siderolite, Atacama	Na	K	..	..	Cu	Ag	..	Ca	..	..	..	..	..	Fe	Ni	..	Mn	Cr	Pb			

* Lithium was found in all these dusts.

† Bismuth was found in this dust.

in the tabular statement only, but the different kinds of volcanic dust and flue dust were dissolved, and the silica removed, after which the bases were separated into groups, and the spectra of these groups were photographed; each spectrum receives a detailed description preceding the tabulated statement.

Flue Dust.

Plate 386.—Dust from the flue of Crewe gasworks. May 28, 1899 The silica was removed from 1 grm. by treatment with ammonium fluoride.

Spectrum 1.—The insoluble residue contained—
Ca, Sr, Na, Pb, Fe, Cu, Ag, K.

Spectrum 2.—The precipitated yielded by sulphuretted hydrogen—
Pb, Cu, Ag, Ca, Na, Fe, K.

Spectrum 3.—The ammonium hydrate precipitate—
Fe, Ga, Cu, Ag, Pb, In, Ni trace,
Ca, Na, K.

Spectrum 4.—The ammonium sulphide precipitate—
Mn, Na, K, Cu, Ag, Ni, Fe.

Spectrum 5.—The less soluble sulphates—
Ca, Sr, Cu, Na, K.

Spectrum 6.—Magnesia and the alkalis—
Na, K, Ca, Sr, Ni, Rb trace.

Plate 388.—Spectra 4 and 7.—Insoluble residue after treating the dust with hydrochloric acid—
Fe, Ga, Na, K, Ca, Cu, Ag, Ni, Mn.

Plate 347.—Flue dust from Cleveland iron furnaces.

Spectrum 1.—Samuelson's samples, No. 6—
Na, K, Ca, Fe, Rb, Pb, Mn;
traces of Cu, Ag, Ni, Ga, Tl.

Spectrum 2.—Flue dust from basic iron furnace. Samuelson's No. 9—
Na, K, Ca, Fe, Rb, Pb, Mn;
traces of Cu, Ag, Ni, Tl, Ga, In, Cs, Sr.

Spectrum 3.—Flue dust, Gjers, Mills, and Co.—
Na, K, Ca, Fe, Rb, Pb, Mn;
traces of Cu, Ag, Ni, K, Ga, In.

Plate 354—

Spectrum 4.—Flue dust, Gjers, Mills, and Co.—
Fe, Ca, Cu, Mn, Na, K, Pb, Rb;
traces of Ni, Tl, Ag.

Plate 325.—1. Flue dust from Nicholson's copper smelting works, Hunslet, Leeds—
Na, Cu, Pb, Tl, Ag, In, Fe, K,
Ca, Ga, Rb.

Plate 312.—Iron pyrites from coal—
Fe, Cu, Tl, Pb, Ag, and possibly a trace of gallium.

Volcanic Dust.

Specimens received from Professor J. P. O'Reilly.

Plate 311.—*Te Ariki.*—After complete solution of the substance, the heavy metals were precipitated with ammonia and the filtrate with ammonium oxalate, after which the solution containing magnesia and the alkalis was examined.

Spectrum 1.—The ammonia precipitate—
Fe, Ca, Pb, Na, K trace, Ga trace, Cu trace.

Spectrum 2.—The ammonium oxalate precipitate—
Ca, Sr, Mn, traces of Na, K, Pb, Fe, and Ag.

Spectrum 3.—Magnesia and the alkalis—
Na, K, MgO, Mn, Rb, Cu;
Ni the merest trace.

Taurunga.

Plate 311.

Spectrum 4.—The ammonia precipitate—
The constituents are similar to No. 1.

Spectrum 5.—Ammonium oxalate precipitate—
Similar to No. 2.

Spectrum 6.—Magnesia and the alkalis—
Similar to No. 3.

Te Hape-o-Toroa.

Plate 312.

Spectrum 1.—The ammonia precipitate—
Similar to Nos. 1 and 4.

Spectrum 2.—The oxalates—
Similar to Nos. 2 and 5, but the silver was not so strong.

Spectrum 3.—Magnesia and the alkalis—
Similar to Nos. 3 and 6.

It is necessary to explain that the symbol for magnesium and the alkaline-earth metals refers generally to the oxides. With magnesium, in fact, this is always so, since the bands of the oxide magnesia alone are visible. In the case of calcium, the blue line 4226 is photographed when only a small quantity is present, but the bands of calcium oxide are the chief feature of the spectrum when the base is in larger proportion. Where the symbol is printed in italics, it indicates a trace of the substance, and where followed by a note of interrogation it is not quite certain if even a trace is present, as, for instance, where only one or two rubidium lines is seen, there being two iron lines occupying almost the same positions; or where one of the gallium lines is barely visible, and the second is enveloped by manganese lines. The relative strength of the lines, as seen by comparing the different spectra, are, in some instances, indicated on the tabulated statement by suffixes, the number 1 indicating the weakest line, and 10 the strongest.

The difference in the number of the iron lines is a measure of the quantity of iron present as metal or otherwise, and a comparison of the strength of the lines also indicates the relative quantity of substances. The results in many cases are quantitative, inasmuch as the same weight of material was taken.

(To be continued).

COMPOSITION AND NATURE OF THE RED RAIN.

By Dr. T. L. PHIPSON.

The newspapers of various countries of Europe have recently called attention to a red rain which fell between the 11th and 13th of March, 1901, in Sicily, Naples, Leghorn, Venice, Coburg, Hamburg, Schleswig-Holstein, and at Malvern, in Worcestershire.

The deposit left by this rain in the form of an exceedingly fine dust is described as reddish or fawn-coloured, and greasy to the touch. At Leghorn 4½ grms. were swept from the marble table in front of a café, and it was calculated from this that many thousands of tons of this fawn-coloured dust must have fallen throughout Italy between the dates above-mentioned.

I am indebted to Captain C. J. Gray, F.R.G.S., for a small quantity of a precisely similar product that fell with the rain at Melbourne, Australia, on the 12th December, 1896, and I have submitted it to as full an examination as the very minute quantity would allow.

In my recently published work, "Researches on the Earth's Atmosphere," I have alluded to salt rain, and to coloured rain produced by volcanic ash, or desert sand uplifted by the wind and suspended in the air; there have been also blood-red deposits found upon the ground, which consist of cells of the *Protococcus nivalis*, or *Palmella sanguinea*, and similar microscopic plants that have shown themselves after a fall of rain or snow. I have invariably found abundance of unicellular algæ in the first fall of snow in early winter, and the red rain deposit examined formerly by the French chemist Cahours (in

1852), was found to consist of organic cells, and burnt away entirely, leaving little or no residue.

The fawn-coloured dust left by red rain is, on the contrary, of a mineral nature; it is always similar in colour, fineness, and microscopic appearance. I have made a careful examination of this reddish deposit, and the result has been rather unexpected and interesting.

When dry it is of a fawn-colour, rather paler than oxide of cerium, but becomes darker when wet. Under the microscope it is seen to consist of exceedingly minute grains, *mostly flat*, and of various colours; they are also of various shapes and sizes. The largest are about 2/100ths of a m.m.; the greater number are about 5/100ths, and the smallest 5/100,000ths of a m.m. in diameter. The irregularity of their forms gradually disappears as they get smaller, so that to the eye the smallest appear circular. Many are white, and more or less transparent, grey, greenish-grey, slate-coloured; others are yellow, and brown, and translucent; a few are ruby-red, and others are dark and opaque.

When calcined at a red heat this dust darkens, and loses 14·3 per cent of water and organic matter (this is exactly the amount of water and organic matter found in the Orgueil meteorite). On cooling after calcination it becomes fawn-coloured again, and the colours of the grains seen under the microscope have not been much altered by calcination.

When boiled in hydrochloric acid (finally adding a few drops of nitric acid), a notable portion is dissolved, and yields a solution containing *iron*, and other substances, *among which is nickel*.

After this boiling in acid the fawn-colour becomes much darker, similar to the dark crust seen on meteorites where it is very thin. Having placed the existence of nickel in this substance beyond doubt, I am of opinion that it is partly, if not wholly, of cosmic origin, and not merely desert sand uplifted by the wind, nor volcanic dust; it would appear to be the mineral dust left in the higher regions of the air by the explosion of meteors, or shooting stars.

The only thing that makes me hesitate to assert this absolutely is the fact that oxide of nickel has once been said to have been found in the *rapilli* of the Kölerberg, in Silesia, to the extent of 0·1 per cent (the analysis by Zulkowski is given in my work on "Meteors, Aërolites, and Falling Stars," p. 118). In the fawn-coloured products of the red rain I estimate that there is considerably more nickel than that, more than ten times as much; and in the ash or cinders of Etna and Hecla no nickel has ever been found, nor in those of Vesuvius.

I may add to this that both March and December are known to be meteoric "periods."

ANTIMONIATES OF COPPER.

By A. E. DELACROIX.

Ammoniacal Antimoniate of Copper.—Tetra-antimoniate of copper, $(Sb_2O_5)_2CuO$, treated with ammonia, gives, among other products, small blue hexagonal crystals, which, when dried in the air, have the formula $Sb_2O_5,CuO,3NH_3,9H_2O$.

Antimoniate of copper, freshly precipitated from acetate of copper by antimoniate of potash, dissolves completely in dilute ammonia. Crystals, identical in appearance and of the same composition as the preceding, are not long in forming.

If we make use of a precipitate of antimoniate of copper dried on the filter-pump, and concentrated ammonia, there is still solution, after which a deep blue viscous mass is quickly formed, which soon solidifies. The bi-cupric tri-antimoniate, $(Sb_2O_5)_3(CuO)_2$, partially dissolves in ammonia; it then crystallises as cupram monic antimoniate, similar in appearance to the preceding salts.

According to MM. Beilstein and Blaese (*Bull. Acad. de Saint Petersbourg*, vol. xxxiii., p. 100), Raschig has prepared, in another manner, an ammoniacal antimoniate of copper only differing from ours by $3H_2O$.

Antimoniate of Copper and Potash.—Freshly prepared and washed tetra-antimoniate of copper, $(Sb_2O_5)_2CuO$, was treated with potash. After digesting for several days it was again washed by decantation to free the precipitate of the mother-liquor. After the second decantation the green precipitate dissolves in the water added for the third washing. Presuming that the resulting green solution contained a double antimoniate of copper and potash, a part of it was congealed. The salt, in the form of green flakes, was found to consist of $Sb_2O_5CuO_{0\cdot569}K_2O_{0\cdot399}$.

Basic Antimoniate of Copper.—A part of the above-mentioned green solution was heated to 80°. A voluminous precipitate then separated; this was thoroughly washed by thirty-five decantations. Analysis gave for the product dried at 100°, $(Sb_2O_5)_2CuO_4\cdot86,7\cdot06H_2O$. — *Bull. Soc. Chim.*, Series 3, vol. xxv., No. 6.

ON ANTIMONIC ACIDS.

By A. E. DELACROIX.

The Preparation of Antimonic Hydrate.—The method described by M. Senderens (*Bull. Soc. Chim.*, vol. xxi., p. 47), gives a gelatinous precipitate, difficult to wash. By making use of the following modification we obtain a pulverulent hydrate similar to that formed by pentachloride of antimony, and easily washed:—

Dissolve 1 kilogrm. of trichloride of antimony in 1 litre of hydrochloric acid (D = 1·19). The mixture is heated to 100°, and 250 c.c. of nitric acid (D = 1·38), added as quickly as the violence of the reaction will allow.

To prepare the hydrate a certain quantity of the cooled liquid is treated with water.

Preparation of Tetra-antimonic Acid.—We must use heat to get concentrated solutions. The hydrate being rubbed up with water at 50° is then boiled for four or five minutes; the liquid becomes nearly clear; it is then divided up into small portions, and cooled rapidly.

The product does not contain any triantimonic acid. A saturated solution, prepared at 70°, contained 53·89 grms. of Sb_2O_5 per litre, of which only a very small quantity was in the tri-antimonic state. The density of this solution was 1·0497.

The Action of Alkalis and Alkaline-earthy Bases on Tri-antimonic Acid. Soda.—The neutralisation of this acid by soda, in the presence of phthalein, takes place with the formation of $(Sb_2O_5)_3(Na_2O)_2$.

Potash.—In the cold the neutralisation takes place, forming $(Sb_2O_5)_2K_2O$.* The same relation was observed with tetra-antimonic acid, but the salt formed is different. It is not precipitable by alcohol, as is the case with tetra-antimoniate of potash.

The freezing of the acid thus neutralised gives a crystalline powder, for which the formula $Sb_2O_5(K_2O)_{0\cdot53}$ has been found. This antimoniate may be looked upon as a mixed salt, $(Sb_2O_5)_3K_2O.(Sb_2O_5)_3(K_2O)_2$.

I may here mention that the salt $(Sb_2O_5)_3(K_2O)_2$ is formed by the addition of an excess of potash to cold tri-antimonic acid. The triantimonic solution, neutralised as has been described above, becomes acid when it is boiled. However, by alternate neutralisations and boilings we can reach a definite neutralisation expressed by the formula $(Sb_2O_5)_5(K_2O)_4$, a mixture or combination of the bi- and tri-potassic tri-antimoniates, $(Sb_2O_5)_3(K_2O)_2.2Sb_2O_5.K_2O$. After standing for a long time it deposits an amorphous salt, and the clear liquid contains a flocculent antimoniate.

* This corrects an error unfortunately made in the publishing of my first paper on this subject (*Journ. de Pharm. et de Chim.*, [6], vol. vi., p. 337).

Lithia.—With this base we arrive at the same results as with potash. After neutralising hot, there is an iridescent deposit after a few hours, composed of hexagonal tables of $Sb_2O_5Li_2O$.

Ammonia.—No indicator gives any results with this alkali.

Baryta.—Neutralisation in the presence of phthalein in the cold gives $(Sb_2O_5)_5BaO_4$, and when hot, $(Sb_2O_5)_{10}BaO_2$.

The salt $(Sb_2O_5)_5BaO_4$ is also formed by the prolonged action of a large excess of acetate of baryta.

In the presence of luteol and of perezol the neutralisation takes place, forming $(Sb_2O_5)_3(BaO)_2$.

Strontia and Lime.—The reaction, which is slow with baryta, is still more so with strontia and with lime. The results are less marked, but appear to be the same.

With methyl-orange the alkaline earths give results very closely approaching those given by luteol.—*Bull Soc. Chim.*, Series 3, vol. xxv., No. 6.

EIGHTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED IN 1900.*

By F. W. CLARKE.

DURING the year 1900, fewer new determinations of atomic weight than usual have appeared. The data are given in the following pages, together with Herzfeld's research upon calcium, which appeared three years ago. It was unfortunately published through an unusual channel, and was therefore overlooked at the time. Attention may also be called to the Presidential Address (*Journ. Am. Chem. Soc.*, xxii., 51) of Professor Morley before the American Chemical Society, which is a valuable discussion of the probable accuracy of our knowledge as to the ratio between hydrogen and oxygen.

Nitrogen.

Dean's research (*Journ. Chem. Soc.*, lxxvii., 117) upon the atomic weight of nitrogen, which was noticed in abstract in the report for 1899, has now appeared in full. Weighed quantities of silver cyanide were dissolved in nitric acid, and the nitrate solutions were titrated with a standard solution of potassium bromide. As the latter was not absolutely pure its silver value was independently determined, and the titrations give therefore the quantity of silver proportional to the cyanide. The last experiment of the series was made by solution of the cyanide in sulphuric acid instead of the nitric acid previously used. Attempts to reduce silver cyanide in hydrogen gave unsatisfactory results, due to the formation of paracyanogen and silver carbide. The final data are subjoined.

Weight of AgCN.	Weight Ag.	Equivalent of CN.
6·2671	5·0490	26·039
17·60585	14·18496	26·026
17·1049	13·7801	26·049
17·9210	14·43881	26 030
12·11215	9·75875	26·028
14 6672	11 81727	26·029
Sum, 85·67820	69·02889	26 032

If C=12 001, then N=14·031, the value finally adopted. All weights were reduced to a vacuum standard.

Another determination of the atomic weight of nitrogen has also been announced by Scott (*Proc. Chem. Soc.*, xvi., 205). From ammonium bromide he finds $NH_4Br=97·996$. For the chloride, $NH_4Cl=53·516$. The first value is lower than that found by Stas, the second is in agreement with Stas. The full paper will appear early in 1901.

Calcium.

The following determinations by Herzfeld (*Zeit. des Vereins fur die Rübenzucker-Industrie*, xlvii., Heft 497), made in 1897, were overlooked at the time, and are now recorded here for the sake of completeness. Calcium carbonate was prepared from the bicarbonate, and reduced to oxide by ignition at a temperature of from 1300° to 1400°.

Weight $CaCO_3$.	Weight CO_2.	Weight CaO.	Atomic weight Ca.
3·9772	1·7504	2·2268	39·687
2·3614	1·0396	1·3218	39·655
3·2966	1·4510	1·8456	39·677
		Mean	39·673

Calculated with H=1, C=11·92, O=15·879. With O=16, Ca=39·975.

Iron.

The determinations by Richards and Baxter (*Zeit. Anorg. Chem.*, xxiii., 245) of the atomic weight of iron are based upon the reduction of pure Fe_2O_3 in a current of electrolytic hydrogen. Two series of results are given, representing ferric oxide prepared by two distinct methods. For details of manipulation the original paper must be consulted.

First Series.—Ferric oxide obtained by calcination of ferric hydroxide :—

Weight Fe_2O_3.	Weight Fe.	Atomic weight Fe.
3·17485	2·22096	55·885
3·61235	2·52750	55·916
	Mean	55·900

Second Series.—Ferric oxide obtained by calcination of ferric nitrate :—

Weight Fe_2O_3.	Weight Fe.	Atomic weight Fe.
3·97557	2·78115	55·883
4·89655	3·42558	55·891
4·35955	3·04990	55·891
7·14115	4·99533	55·870
6·42021	4·49130	55·882
	Mean	55·882

Mean of all seven determinations, 55·89, when O=16. With H=1, Fe=55·47. All weights were reduced to a vacuum.

Gadolinium.

Atomic weight determined by Benedicks (*Zeit. Anorg. Chem.*, xxii., 393), by synthesis of the sulphate from the oxide. Data as follows :—

Weight oxide.	Weight sulphate.	At. wt. gadolinium.
0·4308	0·7171	156·57
0·5675	0·9451	156·35
0·5726	0·9534	156 44
0·6785	1·1301	156·29
0·7399	1·2329	156·10
1·3253	2·2063	156·52
	Mean	156·38

Calculated with O=16 and S=32. The final result agrees well with the determination by Bettendorf, who found Gd=156·33.

Thorium.

Atomic weight re-determined by Urbain (*Ann. Chim. Phys.*, [7], xix., 223). The thoria was purified by conversion into the acetyl acetonate, which was crystallised from solution in chloroform. It was then converted into sulphate. The atomic weight determinations (with O=16) were made by calcination of anhydrous $Th(SO_4)_2$. Data as follows :—

Weight sulphate.	Weight ThO_2.	Atomic weight Th.
1·0925	0·6815	233·30
0·5926	0·3699	233·75
1 0230	0·6384	233·58

Calcination of the hydrous sulphate gave lower values, probably because the octohydrated salt used contained traces of the sulphate with 9 molecules of water.

* *Journal of the American Chemical Society*, xxiii., No. 2.

Miscellaneous Notes.

Muthmann and Böhm (*Ber. d. Chem. Ges.*, xxxiii., 42), have prepared pure yttria by fractional precipitation with neutral potassium chromate. The final sample was practically pure, and gave a good atomic weight determination. 2·46585 grms. sulphate yielded 1·19523 grms. of oxide. Hence Yt = 88·97, when O = 16.

Samarium has been studied by Demarçay (*Comptes Rendus*, cxxx., 1185). By synthesis of the sulphate he finds the atomic weight of the metal to range from 147·2 to 148·0, when O = 16. The higher values, about 150, obtained by other investigators, he attributes to the presence of other earths. In a second paper (*Comptes Rendus*, cxxx., 1469) he describes one of these earths, which is intermediate between samarium and gadolinium, with an atomic weight of the metal equal to 151, nearly. This, however, is only a rough approximation, as the oxide was not sufficiently pure for exact work.

The density of krypton has been carefully determined by Ladenburg and Krügel (CHEM. NEWS, lxxxi., p. 205). From it the atomic weight of the element becomes, in two experiments, 58·67 and 58·81, or 58·74 in the average.

Ramsay and Travers (CHEM. NEWS, lxxxii., p. 257) give density determinations and atomic weights for the new gases of the atmosphere as follows:—

	Density.	Atomic weight.
Helium	1·98	3·96
Neon	9·97	19·94
Argon	19·98	39·96
Krypton	40·88	81·76
Xenon	64·00	128·00

Metargon is abandoned, as non-existent. Why the value for krypton should diverge so widely from that found by Ladenburg and Krügel, is unexplained. It will be noticed that most of these gases fall between the halogens and the alkali metals in the periodic system, although argon is still slightly divergent from theory.

Mdme. Curie has continued her studies upon radium (*Comptes Rendus*, cxxxi., 382), which were referred to in the report for 1899). She now describes a radiferous barium chloride in which the mixed metals have a mean atomic weight of 173·6 to 174. In this sample, judging from spectroscopic evidence, there was probably rather more radium than barium.

Table of Atomic Weights.

The following table of atomic weights differs but little from that issued last year. First, your Committee gives its own list, in two columns, representing both standards of value, H = 1, and O = 16. The only change here is in iron, due to the work of Richards and Baxter. Richards's table is unchanged, except in the same item. The table of the German Committee is that which was issued in January, 1901, as an insert to the first number of the *Berichte*.

	Clarke.			
	H = 1.	O = 16.	Richards.	German.
Aluminum ..	26·9	27·1	27·1	27·1
Antimony ..	119·5	120·4	120·0	120·
Argon	?	?	39·9?	39·9
Arsenic	74·45	75·0	75·0	75·
Barium	136·4	137·40	137·43	137·4
Bismuth	206·5	208·1	208·0	208·5
Boron	10·9	11·0	10·95	11·
Bromine	79·34	79·95	79·955	79·96
Cadmium . ..	111·55	112·4	112·3	112·4
Cæsium	131·9	132·9	132·9	133·
Calcium	39·8	40·1	40·1	40·
Carbon	11·9	12·0	12·001	12·00
Cerium	138·0	139·0	140·	140·
Chlorine	35·18	35·45	35·455	35·45
Chromium ..	51·7	52·1	52·14	52·1
Cobalt	58·55	59·00	59·00	59·
Columbium ..	93·0	93·7	94·	94·

	Clarke.			
	H = 1.	O = 16.	Richards.	German.
Copper	63·1	63·6	63·60	63·6
Erbium	164·7	166·0	166·	166·
Fluorine	18·9	19·05	19·05	19·
Gadolinium ..	155·8	157·0	156·?	156·
Gallium	69·5	70·0	70·0	70·
Germanium ..	71·9	72·5	72·5	72·
Glucinum ..	9·0	9·1	9·1	9·1
Gold	195·7	197·2	197·3	197·2
Helium	?	?	4·0?	4·
Hydrogen ..	1·000	1·008	1·0075	1·01
Indium	113·1	114·0	114·	114·
Iodine	125·89	126·85	126·85	126·85
Iridium	191·7	193·1	193·0	193·
Iron	55·5	55·9	55·9	56·
Krypton	—	—	—	81·8
Lanthanum ..	137·6	138·6	138·5	138·
Lead	205·36	206·92	206·92	206·9
Lithium	6·97	7·03	7·03	7·03
Magnesium ..	24·1	24·3	24·36	24·36
Manganese ..	54·6	55·0	55·02	55·
Mercury	198·50	200·0	200·0	200·3
Molybdenum ..	95·3	96·0	96·0	96·
Neodymium ..	142·5	143·6	143·6	143·6
Neon	—	—	—	20·
Nickel	58·25	58 70	58·70	58 7
Nitrogen	13·93	14·04	14·045	14·04
Osmium	189·6	191·0	190·8	191·
Oxygen	15·88	16·000	16·0000	16·00
Palladium ..	106·2	107·0	106·5	106·
Phosphorus ..	30 75	31·0	31·0	31·
Platinum	193·4	194·9	195 2	194·8
Potassium ..	38·82	39·11	39·140	39·15
Praseodymium.	139·4	140·5	140·5	140·5
Rhodium	102·2	103·0	103·0	103·
Rubidium ..	84·75	85·4	85·44	85·4
Ruthenium ..	100·9	101·7	101·7	101·7
Samarium ..	149·2	150·3	150·0	150·
Scandium ..	43·8	44·1	44·	44·1
Selenium	78·6	79·2	79·2	79·1
Silicon	28·2	28·4	28·4	28·4
Silver	107·11	107·92	107·930	107·93
Sodium	22·88	23·05	23·050	23·05
Strontium ..	86·95	87·60	87·68	87·6
Sulphur	31·83	32·07	32·065	32·06
Tantalum ..	181·5	182·8	183·	183·
Tellurium ..	126·5	127·5?	127·5?	127·
Terbium	158·8	160·	160·	—
Thallium	202·61	204·15	204·15	204·1
Thorium	230·8	232·6	233·	232·5
Thulium	169·4	170·7	170·?	171·
Tin	118·1	119·0	119·0	118·5
Titanium	47·8	48·15	48·17	48·1
Tungsten . ..	182·6	184·	184·4	184·
Uranium	237·8	239·6	240·	239·5
Vanadium ..	51·0	51·4	51·4	51·2
Xenon	—	—	—	128·
Ytterbium ..	171·9	173·2	173·	173·
Yttrium	88·3	89·0	89·0	89·
Zinc	64·9	65·4	65·40	65·4
Zirconium ..	89·7	90·4	90·5	90·7

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 1st inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Mr. J. H. Batten, Dr. R. Barnes, Dr. R. L. Bowles, Mr. G. L. Johnston, Mr. J. Lawrence, and Mr. E. T. Sturdy were elected Members. The special thanks of the Members were returned for a donation of £50 from "A Friend" to the Fund for the Promotion of Experimental Research. It was announced from the Chair that His Majesty The King had graciously consented to become a Patron of the Royal Institution.

A BIBLIOGRAPHY OF STEEL WORKS ANALYSIS.

Part VIII.
VANADIUM AND TITANIUM.

By HARRY BREARLEY.

(Continued from p. 64).

VANADIUM.

I. Separation from other Elements.

Iron (or Al).—

1079. Bettendorf (*C. N.*, xxxvii., 113).—AmHO precipitates vanadate of Al, which is decomposed by Am_3PO_4, the V passing into solution. The reaction with ferric salts is similar.

1080. Carnot (*C. N.*, lvi., 16).—Fe is separated by repeated precipitations with AmHO, acetate, or H_2S; not so Cr or Al.

1081. Bamber (Process 953).—Separates Va and Fe. (See also 1112).

1082. Helouis (*J. S. C. I.*, 1896, 657).—From Al-Va alloys the Al is dissolved by HCl. The residual Va is not attacked by HCl or alkalis. Influence of Va on physical properties of irons.

Chromium.—

1083. Classen (*J. C. S.*, l., 428).—Fuse the mixed oxides with Na_2CO_3 and S; the Cr remains as oxide. Analytical characters of insoluble Va compounds of Pb, Ba, and NH_4 given.

1084. Klecki (*C. N.*, lxix., 54).—The V is precipitated from acetic solution with Ur; the chromate is easily soluble.

Arsenic.—

1085. Field and Smith (*C. N.*, lxxv., 26).—Heat the mixed sulphides below 250° in HCl gas; As is volatilised. As oxides, both metals volatilise, and are thus separated from vanadinite.

1086. Friedheim and Michaelis (*J. C. S.*, lxviii., ii., 415).—Eliminate As by distilling with methyl alcohol and HCl, after adding SO_2 to form V_2O_4. (See also 1098).

1087. *Titanium.*—Deville (*C. N.*, iii., 226).—Fuse rutile with $KHO+KNO_3$, leach, filter, pass H_2S, and drive H_2S from acidified filtrate; Va is precipitated. Used (*C. N.*, v., 86) for estimating Va in cryolite.

1088. *Uranium.*—Lallemand (*C. N.*, xliii., 72).—The filtered nitric acid solution of pitchblende is precipitated with Na_2CO_3. Ur in solution; Fe, Va, W, &c., precipitated (see 1112).

1089. *Zinc.*—Halberstadt (*C. N.*, xlvii., 101).—Evaporate HCl solution, digest with Am oxalate, and boil with acetic acid. Va is dissolved; Zn, Ba, Ca, and Pb are precipitated.

1090. *Gallium.*—Boisbaudran (*C. N.*, xlviii., 86).—From HCl solution mixed with As_2O_3 and Am acetate, Ga is precipitated by H_2S; or mix neutral solution with Am_2S, and precipitate V with HCl.

II. Gravimetric Estimation of Vanadium.

1091. Phipson (*C. N.*, vii., 210).—Fuse clay ironstone with KNO_3, add KHO to filtrate, then H_2S, and precipitate sulphovanadate with HNO_3 and $BaCl_2$. Decompose precipitate with H_2SO_4, and precipitate as ammonia salt. Some French processes described. TiO_2 interferes with the microcosmic blowpipe test (1122).

1092. Riley (*C. N.*, viii., 261 and 277).—When solution of iron is evaporated, Va accompanies Ti and Si. Va is precipitated with Fe on adding AmHO. On boiling $KHSO_4$ fusion, Va is precipitated with the basic sulphate. Dissolve Fe in HCl, wash residue with KHO, and burn off C; the final residue nearly pure V oxides.

1093. Classen (*C. N.*, lv., 74).—Digest magnetite with H_2SO_4, drive off SO_3, fuse with Na_2CO_3+S, precipitate as sulphovanadate by acidifying, and weigh as V_2O_5; Cr remains insoluble.

1094. Gerland (*C. N.*, xxxvi., 29).—V precipitated with AmCl, carries down K but not Na salts.

1095. Pope (*J. I. S. I.*, 1899, ii., 489).—Fuse ore with $NaNO_3$, precipitate with Ba, dissolve in H_2SO_4, convert to $AmVO_3$, and ignite to V_2O_5.

1096. Ditte (*C. N.*, lv., 203).—Precautions in precipitating, washing, and igniting $AmVO_3$ so as to avoid loss through solubility, volatility, &c.

1097. Boettger (*C. N.*, xxix., 62).—Heat ore with nitre and soda, leach, nearly neutralise with HNO_3, and precipitate V with $Ba(NO_3)_2$.

1098. Carnot (*C. N.*, lvi., 35).—V is completely precipitated from alkaline solutions as dibarium vanadate, and may be thus ignited. P, As, and partially W and Mo, are precipitated free from Va by substituting Sr for Ba.

1099. Gerland (*C. N.*, xxxvi., 271).—Va is almost quite precipitated with PbA_3. Decompose precipitate with HNO_3, add H_2SO_4, and ignite evaporated filtrate to V_2O_5 (readily reduced by dust and flame gases).

1100. Carnot (*C. N.*, lvi., 42).—Hg', Hg'', Pb, and Bi solutions all completely precipitate Va from neutral or faintly alkaline solution. Precipitates can also be formed with Co, Ni, Zn, Cd, and Cu.

1101. Carnot (*C. N.*, lvi., 16).—V precipitated with uranium nitrate is free from alkaline earths, Zn, Mn, Cu, &c. P, As, W, and Mo interfere. The ignited precipitate contains 24·22 per cent V. MnO solutions also precipitate V quantitatively; Mo does not interfere.

1102. Rosenheim and Friedheim (*C. N.*, lxvi., 27).—Difficulties of estimating V in the presence of As, P, Mo, and W. Weighs the CO_2 evolved in the reaction $V_2O_5+H_2C_2O_4=V_2O_4+H_2O+2CO_2$. Above elements do not interfere.

III. Volumetric Estimation of Vanadium.

1103. Genth (*C. N.*, xxxiv., 79).—Reduce to V_2O_4 with SO_2; oxidise to V_2O_5 with permanganate. Excess of H_2SO_4 without influence.

1104. Gerland (*C. N.*, xxxvi., 272).—As 1103. The *first* appearance of the pink colour is the final point. $KMnO_4$ can be repeatedly standardised by pure V compounds.

1105. Osmond and Witz (*C. N.*, xlvii., 12).—Slag decomposed with H_2SO_4, permanganate added to faint colour, and then standard $FeSO_4$, using ferricyanide indicator. Excess H_2SO_4 should be considerable. Also by comparing colour of hypovanadic solutions.

1106. Ditte, Carnot, &c. (*C. N.*, lxviii., 77, 89, &c.).—Separation of Ba and Sr from Va. Process 1103 is not affected by Mg, Ca, or (with modification) W. Analysis of vanadio-tungstates. (See also 227 to 230).

1107. Rosenheim (*J. S. C. I.*, 1891, 164).—The titration of V_2O_4 with $KMnO_4$ is obscured by a violet colouration when WO_3 is present.

1108. L'Hote (*C. N.*, lv., 191).—The ore mixed with C is heated in Cl. Vanadyl chloride is condensed and titrated with $KMnO_4$ in hot solution after reducing with zinc (see 1131).

1109. Stead (*J. I. S. I.*, 1893, i., 164).—In the presence of CrO_3, titrate with $FeSO_4$ and $KMnO_4$, which gives Va+Cr, and then with $FeSO_4$ and $K_2Cr_2O_7$, which gives Va only. V_2O_4 is not oxidised by $K_2Cr_2O_7$.

1110. Ridsdale (*J. S. C. I.*, 1888, 73).—Va in slags estimated by modification of 1105. Separation of various constituents of slag, and relative tendency of precipitates to carry down V_2O_5.

1111. Hillebrand (*C. N.*, lxxviii., 217 and 295).—Neither Cr_2O_3 nor H_3PO_4 affect process 1103; Mo and As do. Describes H_2O_2 test.

1112. Fritchle (*C. N.*, lxxxii., 258).—Fe and Ur are precipitated free from V by Na_2CO_3+NaHO. The V in carnotite is found indirectly by estimating the Ur, the Fe+V, and then Fe+Ur+V by permanganate.

1113. Holverscheit (*J. C. S.*, lviii., 1343).—The precipitated Ba or Pb salt is boiled with HCl and KBr. The liberated Br is estimated iodometrically.

1114. Browning (*C. N.*, lxx., 205).—Reduce to V_2O_4 with tartaric acid, alkalise with $NaHCO_3$, add excess of iodine, and titrate with As_2O_3.

1115. Browning and Goodman (*J. C. S.*, lxxii., ii., 234).—Above process interfered with by Mo (not W) unless the reduction with tartaric acid is effected slowly in the cold.

1116. Browning (*C. N.*, lxxiv., 203).—Reduce acid V_2O_5 solution with HI or HBr, and titrate as 1114.

1117. Friedheim (*C. N.*, lxxv., 125).—In 1116 it is better to collect the liberated halogen and estimate as 1113. In the presence of syrupy H_3PO_4, the reduction may be carried to V_2O_3.

1118. Klecki (*J. C. S.*, lxvi., ii., 162).—Dextrose added to a sulphuric solution of V in the presence of Fe gives a green colouration from which the V may be approximately deduced.

1119. Maillard (*C. N.*, lxxxii., 19). — Ether saturated with H_2O_2 is added and the colour compared with standards. Heavy metals may be removed by H_2S or Am_2S, and soluble alkaline salts do not interfere.

IV. Detection of Vanadium.

1120. Deville (*C. N.*, iv., 241).— The sulphovanadite formed on passing H_2S through an alkaline solution is a very delicate test for Va. In *C. N.*, v., 103, it is used for approximately estimating V in cast-iron.

1121. Apjohn (*C. N.*, xxvi., 183).—Fuse mineral with Na_2CO_3, remove SiO_2 and metals precipitable with H_2S, and apply 1120.

1122. Deville (*C. N.*, v., 86).—Tested with P salt, V gives intense green in the R. F., yellow in the O. F. (See 1091).

1123. Sonstadt (*C. N.*, xxvi., 215).—If strong KIO_3 be added to sea-water, V can be detected in the precipitate by blowpipe reactions.

1124. Guyard (*C. N.*, xxxiii., 71).—Add salt of aniline and a chlorate to HCl solution; rapid formation of aniline-black = V.

1125. Witz and Osmond (*C. N.*, liii., 252).—Soak prepared calico strips in solution to be tested, and compare with standard strips after treating with aniline-black mixture minus the hypovanadate.

1126. Hayes (*C. N.*, xxxi., 167).—Gall forms a greenish black precipitate in acid V solutions. In the presence of MnO, AmHO gives a blue solution, like Cu.

1127. Smith (*C. N.*, lxi., 20).—Add dilute ferrocyanide to H_2SO_4 solution; a green colour = V. Both NaHO and KHO may contain V.

1128. Elbram (*J. C. S.*, lxxii., ii., 522).—Faintly acid solution of KCNS gives a yellow colour; more strongly acid, a blue colour with V.

1129. Levy (*J. C. S.*, lii., 305).—The dark green colour given by V_2O_5 with resorcinol distinguishes it from MoO_3 or P_2O_5.

1130. Stead (*J. I. S. I.*, 1893, i., 170).—V is always present in British chromiferous pig-irons. Detects with H_2O_2.

V. Miscellaneous.

1131. Roscoe (*C. N.*, xvii., 135).—In acid solution, zinc forms V_2O_2; magnesium, V_2O_3; and SO_2 or H_2S, form V_2O_4. The relation of V to N, P, As, Sb, &c.

1132. Roscoe (*C. N.*, xx., 37).—V is insoluble in HCl, soluble in H_2SO_4+HF or HNO_3, and fused with formation of vanadates.

1133. Genth and Vom Rath (*C. N.*, liii., 218).—Outline of process for analysis of V minerals containing Pb, Cu, Zn, Mn, Fe, As, P, &c.

1134. Hintz and Weber (*C. N.*, lxx, 157).—How to precipitate V with AmCl; precipitation with Ba in the presence of alkaline salts; and the main portions of 1101 and 1106.

1135. Cowper-Coles (*C. N.*, lxxix., 147). — Electrodeposition of V. Some chemical properties and commercial uses.

1136. Read (*J. C. S.*, lxv., 314).—At high temperatures V_2O_5 gives off O. It readily re-oxidises on cooling. V_2O_4 crystals may be thus obtained.

1137. Witz and Osmond (*J. I. S. I.*, 1882, 770).—V concentrates in (notably the Thomas-Gilchrist) slags.

(To be continued).

SOME PRINCIPLES AND METHODS OF ROCK ANALYSIS.*

By W. F. Hillebrand.

(Continued from p. 151).

Methods aiming at the more or less Direct Estimation of Aluminum.

After First Removing Iron as Sulphide.

Should it be desirable for any reason to effect an actual separation of aluminum, this may best be done, up to a certain point, after the bisulphate fusion (p. 150), by removal of the iron† by ammonium sulphide in ammonium tartrate solution, evaporation of the filtrate, ignition of the residue with sodium carbonate and nitrate, and extraction with water, whereby titanium and zirconium are left on the filter as sodium salts, while chromium and vanadium are carried into the filtrate as chromate, and vanadate along with aluminum and phosphorus. The further separation of the last two from the chromium and vanadium is outlined under "Phosphorus." (See *prox.*). This is as far as the separation can well be carried, and the Al_2O_3 must still be found by subtracting the P_2O_5 from the combined weights of the Al_2O_3 and P_2O_5. The possibility of loss of some P_2O_5 by volatilisation‡ during the bisulphate fusion must be borne in mind here, for if it takes place the final weight of $Al_2O_3+P_2O_5$ will not contain all the P_2O_5.

Some writers recommend dissolving the ignited alumina, iron oxide, &c., in hydrochloric acid, but when the precipitate has been heated over the blast, as it should be, this is very ineffective.

By Extraction with a fixed Caustic Alkali.

A favourite practice in some countries of Europe is to fuse the ignited precipitate containing Al_2O_3, Fe_2O_3, TiO_2, P_2O_5, &c.—or that of the Al_2O_3, TiO_2, P_2O_5, &c., after separation of iron by ammonium sulphide in tartrate solution—with sodium hydroxide in a silver crucible, or to boil the freshly precipitated mixture with a solution of the alkali, on the assumption that the titanium oxide is hereby rendered wholly insoluble, and thus separated from the

* *Bulletin of the United States Geological Survey*, No. 176.

† This being first reduced to the ferrous condition by hydrogen sulphide in acid solution in order to obviate the possibility of precipitating some titanium, which otherwise is likely to happen. (Cathrein, *Zeit. fur Kryst.*, 1882, vol. vi., p. 246; and 1883, vol. viii., p. 259).

‡ H. Rose speaks of such loss when volatilising sulphuric acid in sulphuric acid in presence of phosphoric acid. (*Handb. f. Quant. Anal.*, Finkener Edition, vol. ii., p. 575, and elsewhere).

alumina. This, however, is in part an error, long since pointed out by Gooch (*Proc. Amer. Acad. Arts and Sci.*, 1885, vol. xii., p. 436; *Bull. U.S. Geol. Survey*, No 27, pp. 16 and 17), who showed that pure titanic oxide is markedly soluble under both conditions of treatment. Experiments very recently made by the writer to test the extent of this error brought out the following interesting results:—

When 0·045 grm. of titanic oxide was fused by itself with sodium hydroxide, the clear aqueous extract of the fusion held 0·0031 TiO_2, or about 7 per cent, determined colorimetrically. When freshly precipitated and boiled with the alkali the solubility was less. When fused with sodium carbonate but an infinitesimal trace was dissolved, which required strong concentration for its detection. When mixed with a large excess of alumina and fused with the caustic alkali, the solubility was still very marked, though less than when alumina was absent. With a large excess of ferric oxide, with or without alumina, no titanium could be detected in the unconcentrated filtrate.

It thus appears that fusion with caustic alkali after first removing iron involves an error in the gravimetric determination of both aluminum and titanium which does not appear if the iron has not been removed.

Direct Precipitation of Alumina.

A recent and promising method for the "direct determination of alumina in presence of iron, manganese, calcium, and magnesium," is that of Hess and Campbell (*Journ. Amer. Chem. Soc.*, 1899, vol. xxi., p. 776; Chem. News, 1900, vol. lxxxi., p. 158), but, as with the methods just considered, it involves finally weighing aluminum and phosphorus together, and the behaviour of titanium has not been investigated. For this latter reason the details of the method will not be given. Suffice it to say that precipitation of the aluminum and phosphorus is made by phenylhydrazine, after first neutralising the (preferably chloride) solution by ammonia, and reducing iron by a saturated solution of ammonium bisulphite. Phenylhydrazine "precipitates aluminum from its solutions quantitatively as the hydroxide without a trace of the precipitate being re-dissolved in excess of the precipitant."

IX. *Manganese, Nickel, Cobalt, Copper, Zinc.*

Ammonia is added to the flask containing manganese, the earths, &c. (p. 150), and hydrogen sulphide gas is introduced, whereby manganese, nickel, cobalt, copper, zinc, and a small part of the platinum from the dish are precipitated. The flask is set aside, corked for at least twelve hours, and preferably twenty-four, or even longer; the precipitate, collected and washed on a small filter with water containing ammonium chloride and sulphide, is extracted by hydrogen-sulphide water acidified with one-fifth its volume of hydrochloric acid (sp. gr. 1·11), manganese and zinc, if present, going into solution.

Manganese and Zinc.

The filtrate is evaporated to dryness, ammonium salts are destroyed by evaporation with a few drops of sodium-carbonate solution, hydrochloric and a drop of sulphurous acids are added to decompose excess of carbonate, and to dissolve precipitated manganese, and the latter is re-precipitated at boiling heat by sodium carbonate after evaporation of the hydrochloric acid. If zinc is present, it can be separated from the manganese after weighing. For the small quantities of manganese usually found the sodium-carbonate method of precipitation is to be preferred to that by bromine or sodium phosphate, as equally accurate, and a great time saver.

The precipitation of manganese in alkaline solution by hydrogen peroxide, as proposed by Jannasch and Cloedt (*Zeit. fur Anorg. Chem.*, 1895, vol. x., p. 405), a method which appeared to be simple and accurate, besides affording a separation from zinc, has been shown by Friedheim and Brühl (*Zeit. für Anal. Chem.*, 1899, vol. xxxviii., p. 681), to be valueless, as also other separation methods of Jannasch based on the use of hydrogen peroxide.

The employment of ammonium sulphide instead of bromine for the separation of manganese from the alkaline earths and magnesia has the advantage that, by a single operation, nickel, copper, and zinc are likewise removed if present. There need be no fear of overlooking nickel or copper, for under the conditions of the precipitation they are not held in solution. Now and then a trace of alumina may be found in the precipitate, and magnesia, too, would contaminate it if ammonium salts were not present in sufficient quantity. Regard must therefore be had to these possibilities, and also to the rather remote possibility of the presence of rare earths which were not thrown out by the basic acetate precipitation. (See footnote, p. 150).

Nickel, Cobalt, Copper.

The paper containing these is incinerated in porcelain, dissolved in a few drops of aqua regia, evaporated with hydrochloric acid, the copper and platinum thrown out warm by hydrogen sulphide, and nickel and cobalt thrown down from the ammoniacal filtrate by hydrogen sulphide. This is then rendered faintly acid by acetic acid, and allowed to stand. The sulphide of nickel is simply burned and weighed as oxide, its weight being always very small, and is then tested for colbalt in the borax bead.

It is somewhat unsafe to consider traces of copper found at this stage to belong to the rock if the evaporations have been conducted, as is usually the case, on a copper water-bath, or if water has been used which has been boiled in a copper kettle, even if tinned inside. Therefore, and because of its contamination by a little platinum, it is better to determine copper in a separate portion if its presence is indicated with certainty. (See p. 138).

X. *Calcium and Strontium (Barium).*
Separation from Magnesium.

Precipitation and Ignition of the Oxalates together.—The platinum derived from the dish in the silica evaporation, except for the small portion precipitated with the manganese sulphide, is now wholly in the filtrate from the latter. Its separation at this or any other stage is quite unnecessary; nor is the removal of ammonium chloride usually demanded, since there is no undue amount present in most cases, the first precipitation of alumina, &c., having been by sodium acetate.* Therefore, without destroying ammonium sulphide the calcium and strontium are thrown out by ammonium oxalate at boiling heat, the precipitate, often darkened by deposited platinum sulphide, is ignited and re-dissolved in hydrochloric acid, boiled with ammonia to throw out traces of alumina sometimes present, and re-precipitated as before, but in a small bulk of solution. It is weighed as oxide, transferred to a small flask of 20 c.m.³ capacity, dissolved in nitric acid, evaporated to dryness at 150 to 160° C., and the separation of strontium from calcium effected by ether-alcohol as described below. (See Fresenius, *Zeit. fur Anal. Chimie*, 1893, vol. xxxii., pp. 189, 312, for the latest improvements in this method).

The weight of strontia found deducted from that of the two oxides gives that of the lime.

Necessity for two Precipitations by Ammonium Oxalate.—It may be said with regard to the separation of calcium from magnesium that two precipitations by ammonium oxalate are essential to the attainment of correct results, not only for the complete removal of magnesium but of sodium as well, the retention of compounds of the latter element by calcium oxalate being now generally known. For the treatment of the filtrates, see "Magnesium," *prox.*

* If two or three precipitations by ammonia alone are depended on, the second and third filtrates are evaporated rapidly to dryness, and the ammonium salts removed by ignition.

Separation of Strontium (Barium) from Calcium by Ether-alcohol.

The thoroughly dried nitrates are treated with as little (rarely over 2 c.m.³) of a mixture in equal parts of absolute alcohol and ether as may be needed to dissolve the calcium salt, solution being hastened by occasional gentle agitation. After standing over night in a corked flask the insoluble matter is collected on the smallest possible filter, and washed with more of the above mixture of alcohol and ether. After drying a few c.c. of hot water are passed through the filter, on which may remain a few tenths of a m.grm. of residue which does not usually contain any lime or other alkaline earth, and whose weight is therefore to be deducted from that of the lime, unless it can be shown that it is derived from the glass of the little flask in which the nitrates of calcium and strontium were evaporated. To the solution of strontium nitrate in a small beaker sulphuric acid and then alcohol is added, whereby the strontium is precipitated as sulphate, in which form it is weighed and then tested spectroscopically as to freedom from calcium and barium.

Because of the slight solubility of strontium nitrate in amyl alcohol the method of Browning (*Amer. Journ. Sci.*, 1892, Series 3, vol. xliii., pp. 50, 314), does not appear to be adapted to the separation from calcium of the small amounts of strontium met with in rocks, though with barium the case is different, since its nitrate according to Browning is insoluble in absolute amyl alcohol.

Behaviour of Barium.

Barium will, after two ammonium oxalate precipitations, never be found with the ignited calcium and strontium in more than spectroscopic traces, unless originally present in excess of 3 or 4 m.grms., and very often only when in considerable excess (W. F. Hillebrand, *Journ. Amer. Chem. Soc.*, 1894, vol. xvi., p. 83; CHEM. NEWS, 1894, vol. lxix., p. 147). If present with them, however, it will be separated with the strontium by ether-alcohol or amyl alcohol, and these two must then be treated by the ammonium-chromate method, given below, in order to arrive at the strontium. The barium is best estimated in a separate portion. (See "Barium," *prox.*).

Separation of Barium from Strontium.

Fresenius has shown (*Zeit. fur Anal. Chemie*, 1890, vol. xxix., p. 428), in what manner only a correct separation of barium and strontium can be made by the ammonium-chromate method, involving double precipitation when the amounts are at all large. This procedure is here given for the amounts used by him, but a single precipitation will suffice for the small amounts met with in rock analysis. The volumes of solutions used should be largely reduced, and the operations otherwise shortened.

The chlorides corresponding to 0·2774 grm. BaO and 0·4864 grm. SrO were dissolved in 300 c.m.³ of water with addition of 6 drops of acetic acid (1·065 sp. gr.). To the hot solution was added an excess (10 c.m.³) of ammonium chromate solution (1 c.m.³ = 0·1 grm. neutral chromate). After settling and cooling for an hour the precipitate was washed, mainly by decantation, with water holding ammonium chromate till the filtrate gave no precipitate with ammonia and ammonium carbonate (100 c.m.³ used). The washing was continued with warm water till silver nitrate gave but a very slight reddish colouration (110 c.m.³). The precipitate was then washed into the precipitating dish, the filter rinsed with warm dilute nitric acid (1·2 sp. gr.), and more nitric acid (2 c.m.³ in all added) to the dish. The solution having been diluted to 200 c.m.³ and heated, 5 c.m.³ of ammonium acetate solution (1 c.m.³ = 0·31 grm. ammonium acetate) was very gradually added, and then ammonium chromate till the odour of acetic acid had wholly disappeared (10 c.m.³). After one hour the supernatant liquid was passed through the filter, and the precipitate digested with hot water, which was then cooled; thereupon the precipitate itself was brought on the filter and washed with cold water till silver nitrate gave a scarcely perceptible reaction. The strontium was thrown down from the filtrate by ammonia and ammonium carbonate, after concentration in presence of a little nitric acid, and weighed as carbonate; or the carbonate can be re-dissolved, precipitated by sulphuric acid and alcohol, and weighed as sulphate. The barium is weighed as chromate after ignition, the filter being burned separately.

(To be continued).

CORRESPONDENCE.

MARSH'S TEST FOR ARSENIC.

To the Editor of the Chemical News.

SIR,—The preparation of the material for the production of the little book which has just been published has led me to make an interesting observation on the action of Marsh's test for arsenic. It is this, viz., that even the description of this test in so admirable a work as the "Dictionary of Chemistry," edited by Watts, is misleading and inadequate. Marsh's test (when it is properly worked), is applicable to thick soup, port wine, porter, gruel, tea, coffee, and other alimentary liquors, without as a preliminary operation resorting to the destruction of the organic matter.

It is notorious that the very contrary of all this has been recently put forward on what is termed "high authority."

The explanation is that the original Marsh's test, as it left the hands of its discoverer in the year 1836, was capable of accomplishing the task; but that, in the hands of other chemists, Marsh's test underwent changes—so-called improvements, which did not improve it—and that, as a result of these changes, the so-called Marsh's test as worked in official England is in decay, and cannot accomplish that which Marsh accomplished.

The remedy for such a state of things is the restoring of the text of Marsh's original contribution dating back to the year 1836.

My book contains a reprint of Marsh's paper, and such comparatively slight alterations as are recommended by me tend towards attainment, and not towards the frustration and belittlement of the achievement of Marsh in the year 1836.—I am, &c.,

J. ALFRED WANKLYN.

The Laboratory, New Malden, Surrey.
March 30, 1901.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxii., No. 10, March 11, 1901.

Total Synthesis of Acetylpropylene and Terpilenic Carbides.—M. Berthelot. — During the course of the author's researches on the direct combination of hydrocarbons with one another, he particularly noticed the reaction of acetylene on ethylene and the formation of acetylethylene by the union of equal volumes of these gases. He has since studied the analogous combination of propylene with acetylene, $C_2H_2+C_3H_6=C_5H_8$. This latter reaction is important on account of its forming a method of synthesis for the terpilenic carbides, and more generally for the carbides represented by the formula $C_{10}H_{16}$, the latter being formed in considerable quantities in vegetables.

Reduction of Molybdosulphuric Acid by Alcohol.—E. Péchard.—The reduction of acid molybdates gives rise to blue compounds resulting from the combination of molybdic acid and molybdenum dioxide. These com-

pounds are decomposed by alkalis, since they set free the molybdenum dioxide and give an alkaline molybdate. The author has, however, managed to obtain certain blue molybdenum compounds containing the dioxide, which are comparatively stable in presence of alkalis. He dissolved molybdic acid in strong sulphuric acid and then added alcohol in small quantities. A blue liquid resulted which on evaporation deposited blue crystals, some being hexagonal plates and corresponding to the formula—

$$5NH_3.MoO_2SO_3.7MoO_3+8H_2O,$$

the others prismatic crystals having the formula—

$$3NH_3.MoO_2SO_3.7MoO_3+10H_2O.$$

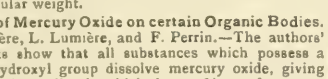
A New Bi-primary Glycol, Butanediol 1 4, or Tetramethylenic Glycol, and its Diacetine.—**J. Hamonet.**—The author's researches on the bi-primary derivatives of butane led him to consider again the question of the synthesis of tetramethylenic glycol. To do this he prepares diacetine of butanediol 1.4—

$$CH_3CO_2CH_2CH_2CH_2CH_2.O_2C.CH_3.$$

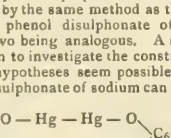
This is a neutral liquid with a pleasant smell. It boils without decomposition at 230° at ordinary pressure. From this again is prepared butanediol 1.4, or tetramethylenic glycol, $HO.CH_2.CH_2.CH_2.CH_2.OH$, a viscous liquid miscible with water in all proportions. It is evident that the constitution of this butanediol and its diacetine can be naturally deduced from that of diiodobutane 1.4, from which each is prepared.

Action of Zinc Powder on Saturated Fatty Acids.—**A. Hébert.**—Zinc powder decomposes the saturated fatty acids, in certain cases into carbon dioxide and water, and in others into carbides of which the major part consists of a mixture of ethylenic carbides of very high molecular weight and boiling point. During this reaction the molecules divide and polymerise at the same time, without apparently giving rise to new bodies related in any way to the original ones. This reaction forms, therefore, an easy method of preparation of the ethylenic carbides of very high molecular weight.

Action of Mercury Oxide on certain Organic Bodies.—**A. Lumière, L. Lumière, and F. Perrin.**—The authors' experiments show that all substances which possess a phenolic hydroxyl group dissolve mercury oxide, giving organometallic bodies in which the reactions of mercury are masked. They have prepared mercury-gaïacol-sulphonate of sodium by the same method as they previously prepared mercury phenol disulphonate of sodium, the properties of the two being analogous. A study of these two bodies led them to investigate the constitution of their molecules. Two hypotheses seem possible, by which the mercury-phenol-disulphonate of sodium can be represented by—



or equally well by—



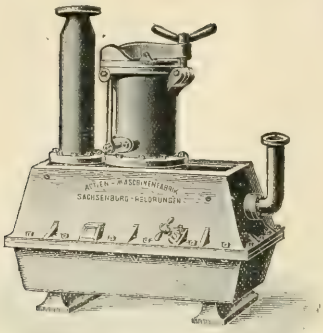
Further experiments will be necessary to decide which of these two is correct.

MISCELLANEOUS.

Royal Institution.—The following are the Lecture Arrangements at the Royal Institution, after Easter:—Dr. Allan Macfadyen, six lectures on "Cellular Physiology, with special reference to the Enzymes and Ferments"; Professor William Knight, two lectures on "The Philosophical Undertones of Modern Poetry" (the Tyndall Lectures); Mr. Roger Fry, two lectures on "Naturalism in Italian Painting"; Sir Alex. Campbell Mackenzie, three lectures on "Arthur Sullivan" (with vocal and instrumental illustrations); Professor Dewar, three lectures on "The Chemistry of Carbon"; Professor W. M. Flinders Petrie, three lectures on "The Rise of Civilisation in Egypt"; Professor J. B. Farmer, two lectures on "The Biological Characters of Epiphytic Plants"; Mr. J. Y. Buchanan, three lectures on "Climate: its Causes and Effects." The Friday Evening Meetings will be resumed on April 19th, when a Discourse will be delivered by Professor J. J. Thomson on "The Existence of Bodies Smaller than Atoms." Succeeding Discourses will probably be given by Dr. Hans Gadow, Mr. Charles Mercier, Professor Jagadis Chunder Bose, Mr. Richard T. Glazebrook, Mr. A. Henry Savage Landor, Earl Percy, M.P., and other gentlemen.

The Chemical Laboratory at Wiesbaden.—During the Winter Term of 1900—1901, the Chemical Laboratory Fresenius was attended by forty-four Students. Of these, twenty-nine were from Germany, five from Austria-Hungary, three from England, two from France, and one from Luxemburg, Italy, Russia, Transvaal, and Rhodesia in South Africa. There were three Assistants in the Instruction-Laboratory, and twenty-four in the Versuchsstationen (private laboratories). In the teaching staff of the institution there has been no change. To this body belong the Directors, Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, Prof. Dr. E. Hintz, and also Dr. Med. G. Frank, Dr. W. Lenz, Dr. L. Grünhut, and (Architect) J. Huber. The Summer Term begins on April 24th. In the Winter Term, 1900—1901, besides scientific work, there were many examinations carried on in the different departments of the private Laboratory (Versuchsstationen) in the interest of trade, industry, mining, agriculture, hygiene, justice, and government.

Preparation and Properties of Non-hydrated Perchloric Acid.—**D. Vorlaender and R. V. Schilling.**—The method of preparation recommended by Roscoe gives only a small return. The authors have modified it by distilling the mixture of H_2SO_4 and $KClO_4$ in vacuo. A mixture of 50 grms. of powdered $KClO_4$ and from 150 to 175 grms. of H_2SO_5 at 96 to 97·5 per cent is heated on the oil-bath in a fractionating flask. Between the pump and the receiver (cooled by a mixture of ice and salt), is placed a tube containing soda-lime; the joints are made with asbestos and water-glass. At a pressure of 50 to 70 m.m. anhydrous perchloric acid passes over at 135—145°. The temperature of the oil-bath is raised successively to 155—160° and to 180—196°. The vapour of $HClO_4$ in vacuo will stand a temperature without decomposition much higher than that given by Roscoe at the normal pressure, viz., 92°. The distilled acid, which is coloured yellow by a little ClO_2, and containing about 1 per cent of H_2SO_4, is immediately afterwards rectified on the water-bath at a pressure of 50—70 m.m., the temperature of the bath being 45—65°; the $HClO_4$ is then collected pure and colourless. It boils at 30° at a pressure of 56 m.m., its density at 22° is 1·764. It does not become solid in a mixture of solid CO_2 and ether. It is insoluble in CCl_4, but dissolves in $CHCl_3$, and this solution takes a red colour in the air, giving crystals of the monohydrate. When kept in sealed flasks it gradually becomes yellow, and then brown, and, finally, decomposes with a violent explosion. When mixed with its own volume of benzene it forms a green emulsion, and then explodes. It also explodes when mixed with phosphoric acid. The stability of $HClO_4$ partly depends on the concentration of the sulphuric acid used in its preparation. The stability increases as the strength of the acid decreases. The use of 98 per cent H_2SO_4 may be dangerous, but with acid at 92—93 per cent perchloric hydrate may distil over and solidify in the tube, blocking it up. Even with a large excess of H_2SO_4 some perchloric acid remains in the flask, as the presence of $KHSO_4$ interferes with the complete decomposition of the $KClO_4$. Phosphoric acid and pyrophosphoric acid do not decompose $KClO_4$.—*Lieb. Ann.*, vol. cccx. p. 369.



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The next Session commences on the 24th of April. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. KREIDEL'S Verlag, at Wiesbaden, or to one of the Directors.

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THE CHEMICAL NEWS.

Vol. LXXXIII., No. 2159

SECOND ANNUAL REPORT OF THE INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS.*

Your commitee upon international action with reference to standard atomic weights, has the honour to submit the following report. Since our report of a year ago (*Journ. Am. Chem. Soc.*, xxii., 70), various other societies have taken part in the discussion; and in the co-ordination of their work, the German Chemical Society has rendered important service. Partly through the initiative of the latter organisation, and partly through the agency of our own Society, a large international committee has been formed, and some of its deliberations are already before the chemical world for consideration.

On March, 30th, 1899, the special committee of the German Chemical Society, Professors Landolt, Ostwald, and Seubert, issued an invitation to other organisations having an interest in chemistry to appoint delegates to the international body. At the December meeting of 1898, the American Chemical Society had already taken action, and your present committee was appointed. The American Academy of Arts and Sciences also designated representatives, and important societies in Germany, Austria Hungary, Belgium, England, Switzerland, Italy, Japan, Holland, Russia, and Sweden also accepted the invitation. A body of 57 representative chemists was thus formed; but France, Norway, and Denmark do not appear in the list. We are informed, however, that the Chemical Society of Paris has recently appointed delegates, and their names will doubtless appear in the next report of the International Committee. Another committee of three was also named by the Fourth International Congress of Applied Chemistry, which met in Paris during the last week of July, 1900.

In October, 1899, the committee of the German Chemical Society sent to each of the international delegates a circular letter proposing three questions. These questions were as follows:—

1. Shall O=16 be fixed as the future standard for the calculation of atomic weights?

2. Shall the atomic weights be given with so many decimals that the last figure is certain within half a unit, or what other procedure shall be adopted?

3. Is it desirable that a smaller committee should be formed, which should undertake the continual revision of the yearly atomic weight table and its publication? In case of agreement upon this point it is proposed that each association shall name a single delegate to the smaller committee.

To these questions forty-nine replies were received. As regards the first question, forty chemists favoured the oxygen standard, seven preferred to retain the hydrogen unit, and two were willing to accept either or both standards. The replies are published in full (*Ber. d. D. Chem. Ges.*, 1900, xxxiii., 1853), some writers giving only categorical answers, and others citing arguments in behalf of the position which they favoured. The majority for the oxygen standard was overwhelming; but, as we shall see later, it has not yet been universally accepted as a final decision. At the Congress of Applied Chemistry, in the section devoted to analytical chemistry, the question was discussed, and in this case the decision of the International Committee was sustained. As only two members of the latter committee were present at this discussion, representing opposite sides, the action of the congress is to be regarded as a ratification of the decision, and not as a mere duplication of votes by the same men. An attempt was made to secure an actual meeting of the International Committee at the congress, but it did not succeed. Too few of its members were in attendance.

The second and third questions of the German Committee were also answered affirmatively, by a large majority in one case, and unanimously in the other. Balloting for the smaller committee has already taken place, and the result will probably be known before this report is presented. As to the second question, the replies and printed criticisms seem to indicate some misunderstanding as to its real significance; and for this reason it ought to receive further and more careful consideration. In the opinion of your committee atomic weights should be printed with so many decimals as have any real significance, even though, in the calculation of ordinary analyses, rounded off values may be employed.

In spite of the great majority given in the International Committee in favour of O=16 as the standard for atomic weights, a vigorous protest against the decision has been made. In the original balloting, the seven dissentients were one American and six German chemists, the latter being delegates from the Verein Deutscher Chemiker. These six chemists, Bredt, Erdmann, F. Fischer, Volhard, Winkler, and Wislicenus, issued a new circular letter (see *Zeit. Angew. Chem.*, July 24th, 1900; Chemical News, August 10th, 1900), addressed to the teachers of chemistry in the German universities and technical schools, asking for a further and fuller expression of opinion. At the date of writing, the result of this canvass has not been published; but Professor Erdmann, in a letter dated November 23rd, 1900, informs us that 143 replies have been received, of which 118 favour the retention of the older standard, H=1. In the new edition of Erdmann's "Lehrbuch der Anorganischen Chemie," this standard is adopted throughout, and other voices have also been raised in protest against O=16. A pamphlet by Lassar-Cohn ("Ueber der Ungeeignete der Newendings für die Berechnung der Atomgewichte vorgeschlagenen Grundzahl 16·000," Hamburg, Voss, 1900), furnishes a case in point, and another paper by Dr. A. R. L. Dohme (*Druggist's Circular and Chemical Gazette*, September, 1900), is noticeable as foreshadowing the probable action of the committee for the decennial revision of the United States Pharmacopœia. In this important work the hydrogen scale is likely to be adopted.

From what has been said so far, it is evident that chemical opinion is still divided on the question of the basis for atomic weights, and that the desired unity of action has not been reached. Neither standard can be forced into general acceptance and further discussion is unavoidable. Even your own committee is divided upon the subject, and therefore asks from the members of the American Chemical Society an expression of their preferences. In order to facilitate such an expression we submit the following summary of arguments which have been used for and against each standard. These may be classified as historical, theoretical, and arguments from convenience,* even though the three categories are not absolutely separable.

Historically, it is urged, the hydrogen unit has the advantage of being the original Daltonian standard; and except temporarily, during the Berzelian period, it has been almost universally recognised. Berzelius made oxygen the standard, and based his scale upon O=100; but oxygen as 16, considered as a basis for atomic weights, is a recent innovation. It is true that the atomic weight of oxygen, referred to hydrogen as unity, was long thought to be 16, but this belief is now known to be an error. To the believer in precedent and priority the adoption of the oxygen standard would seem to be the perpetuation of an error, as well as a break in the historical continuity of science.

* *Journal of the American Chemical Society*, xxiii., No. 2.

* For an elaborate argument in favour of the oxygen standard, see Richards, *Am. Chem. Journ.*, xxiv., 377; see also Brauner, *Zeitschr. Anorg. Chem.*, xxvi., 186.

To the advocates of oxygen as a basis for atomic weights the foregoing argument appears to be irrelevant and fallacious. They claim that hydrogen has only been a nominal unit, since actual determinations of atomic weight are commonly referred to hydrogen through the medium of oxygen, the latter being the experimental standard of reference. To retain the hydrogen scale means to take the ratio H : O as a fundamental base line; and every change in that implies changes throughout the entire table. Historically, at least as viewed from the experimental side of the question, hydrogen has been only the theoretical standard; oxygen, taken as 16, has been the real basis for calculation. The ordinary, familar atomic weights are all in harmony with the oxygen basis, and, with other constants which rest upon the same foundation, they permeate all chemical literature. The retention of the hydrogen unit implies confusion in the interpretation of a great mass of recorded data; and apparent historical conservatism really involves widespread and radical change. After all, the historical argument tends to obscure the essential issue, the true problem being the establishment, on a permanent basis, of the best possible scale.

On theoretical grounds it is claimed that the hydrogen unit is the most natural basis for atomic weights, partly because the hydrogen atom is the lightest atom known, and partly because hydrogen is also the standard for gaseous densities and for valence. The atomic weight scale and the density scale rest upon the same foundations; and if the oxygen standard is adopted, then all vapour-densities must be changed to a corresponding degree. Furthermore, unity, or some number logarithmically equivalent to unity, such as 10 or 100, would seem to be a better starting-point for calculations than some other quantity, arbitrarily chosen, whose selection might be troublesome to explain. An approximate unity, like 1·008, is meaningless, and the value 16·000, taken as a standard, can only be explained by reference back to hydrogen, the unit from which it was originally derived. The explanation, then, is somewhat in the nature of an apology, and concedes much to the opposite side.

To the theoretical arguments the advocates of the oxygen scale attach little importance, regarding the question as one of practice and convenience rather than as one of theory. They point out, however, that elements lighter than hydrogen may yet be discovered, and that then the theoretical considerations would be radically changed. If Prout's so-called law held good, a valid reason for the hydrogen unit would exist; but as matters stand now that unit is as arbitrary as any other, and rests upon no necessary foundation of principle. Which standard, then, is the more convenient for general use?

The answers to this question suggest two quite distinct points of view; that of the teacher on the one hand, that of the laboratory chemist on the other. The teacher argues in favour of the hydrogen unit, that it is easily intelligible to beginners, whereas the oxygen standard is somewhat difficult to explain. The difficulty, moreover, becomes greater when gaseous densities are considered, and the teacher is forced to decide whether he shall adopt a dual standard, or reject the hydrogen basis altogether. A few teachers claim that these difficulties are much overrated, while others propose to evade them, either by giving to the beginner round numbers which are confessedly approximate, or by abandoning hydrogen as a standard of specific gravity, and taking oxygen instead. If the latter policy were followed it might lead to discordance between the allied sciences of chemistry and physics, for the physicist prefers hydrogen as a standard because it is not only the lightest of all substances, but also the one which most nearly approaches the ideal perfect gas. In the hydrogen thermometer its nearly uniform rate of expansion is considered, as well as the fact that at low temperatures it is the last gas except helium to assume the liquid state. The graduation of the hydrogen thermometer is the ultimate standard of reference in all exact thermometry, whether for low temperatures or for high. This question of harmony between different branches of science is one which needs to be seriously considered; and so far, at least as regards our choice of atomic weights, it seems not to have been adequately discussed.

When we consider the use of atomic weights in the calculation of analyses, the oxygen table has the great advantage of familiarity to chemists, and perhaps also the minor advantage that a larger proportion of the values are nearly integers. The latter consideration, however, is of little importance, for many analysts use tables of logarithms or of factors; but to the chemist who employs atomic weights directly, integral numbers are more easily remembered than figures which involve one or two decimal places. In commercial work the ordinary round numbers are likely to hold their own, and no serious inaccuracy of results is to be feared from this practice. The usual errors of analysis far outweigh any uncertainty of calculations which may be due to neglect of decimals in the commoner atomic weights. There are cases to which this argument does not apply, and in which a greater exactness of data is indispensable;* but these are few in number, and should be known to the specialists in whose practice they arise.

The unfamiliarity of the hydrogen scale is easily illustrated by the following table, in which a few of the more common atomic weights, as given under both standards, are compared:—

	H = 1.	O = 16.	Difference.
Hydrogen	1·000	1·008	0·008
Oxygen	15·879	16·000	0·121
Chlorine	35·18	35·45	0·270
Potassium	38·82	39·11	0·290
Copper	63·10	63·60	0·500
Bromine	79·34	79·95	0·610
Silver	107·11	107·92	0·810
Iodine	125·89	126·85	0·960
Barium	136·40	137·40	1·000
Mercury	198·50	200·00	1·500
Lead	205·36	206·92	1·560

The difference increases with increasing atomic weight, and amounts in each case to about 0·75 per cent of the entire value. With small atomic weights the difference appears trifling; in the higher parts of the table the discordance is much more evident.

Clearly then, the adoption of the modern hydrogen scale would compel chemists to drop certain old values and to learn the new. Whether this is desirable or undesirable is for chemists to decide. To the older chemists, who first learned the Daltonian equivalents, and then discarded them for the atomic weights of Cannizzaro, the change will not seem difficult; to the younger men the anticipation of annoyance is likely to be worse than the reality. At all events, the inconvenience, be it great or small, is evident, and it must be taken into account in arriving at the final conclusion.

Your committee hope that the members of the American Chemical Society will consider the questions and considerations which are presented in this report, and express their views upon them. Which system of atomic weights is the better, not merely for temporary purposes, but regarded broadly with a view to the permanent interests of science? That is the real question upon which a consensus of opinion is desired, and which ought to be considered from all points of view. Replies should be addressed to the chairman of this committee, F. W. Clarke, U.S. Geological Survey, Washington, D.C., before June 1st, 1901.

Respectfully submitted,—

F. W. Clarke, Chairman.
J. W. Mallet,
Edward W. Morley,
Theo. W. Richards,
Edgar F. Smith.

* See "Fourth Annual Report of the Committee on Atomic Weights" (*Journ. Am. Chem. Soc.*, xix., 369, May, 1897), with reference to the commercial assay of chrome iron ore.

A BIBLIOGRAPHY OF STEEL WORKS ANALYSIS.

Part VIII.

VANADIUM AND TITANIUM.

By HARRY BREARLEY.

(Continued from p. 164).

TITANIUM.

I. Separation from other Elements.

Iron.—

1138. Streit and Franz (*C. N.*, xxi., 120).—Ti is precipitated by boiling the H_2SO_4 solution, containing considerable acetic acid, free from Fe or Zr.

1139. Baskerville (*J. C. S.*, lxvi., ii., 401).—The separation by boiling is more easy and accurate when the metals exist as chlorides.

1140. Deville (*C. N.*, v., 102).—To H_2SO_4 solution add AmHO, evaporate the whole to dryness, and dissolve out Fe and Al with dilute HNO_3; the residual Ti is calcined and weighed.

1141. Walker (*J. C. S.*, lxxiv., ii., 540).—The Fe is repeatedly precipitated with ammoniacal H_2O_2; Ti in the filtrates.

1142. *Aluminium.*—Gooch (*C. N.*, liii., 55, &c.).—Separation with NaHO or by boiling acid solution inexact. Separate with AmHO and acetic acid, or microcosmic salt and formic acid. Fe is precipitated by H_2S from alkaline tartrate solutions.

Tin.—

1143. Rose (*C. N.*, v., 87).—Fuse oxides with soda and sulphur. The Sn is dissolved out with water.

1144. Hilgar and Haas ((*C. N.*, lxi., 209).—Reduce the mixed oxides in H; dissolve out Sn with HCl. Silicates are decomposed with H_2SO_4+HF (see also Haas, *J. C. S.*, lviii., 1029).

1145. *Silica.*—Holland (*C. N.*, lix., 27).—If H_2SO_4 be not present, Ti is volatilised on treating with HF. Even after two precipitations, TiO_2 contains Fe. TiO_2 dissolves in HCl if Al_2O_3 is also present. A scheme for the analysis of Ti silicates.

1146. *Niobium.*—Marignac (*C. N.*, xvii., 119 and 121).—Fuse the acids with fluorhydride, reduce HCl solution of the melt with zinc, and titrate (Ti only) with $KMnO_4$ (see 1172). Demarçay (*J. C. S.*, xlviii., 639) treats the HF solution of the oxides (including Zr) with KHO short of alkalinity; the Ti remains in solution.

1147. *Gallium.*—Boisbaudran (*C. N.*, xlviii., 164).—Precipitate Ti with KHO from boiling solution. Four other methods given.

II. Gravimetric Estimation of Titanium.

1148. Scheerer (*C. N.*, i., 143).—Decompose silicate as usual, vaporise SiO_2 with HF, and add the residue to precipitate formed in the filtrate with AmHO. Fuse with $KHSO_4$, reduce Fe with H_2S, and precipitate TiO_2 by boiling.

1149. Tosh (*C. N.*, xvi., 168).—Solution and residue treated as 1148. Precipitate Fe and Ti from solution of $KHSO_4$ fusion with AmHO, dissolve out Fe with Am_2S and SO_2, and weigh residual TiO_2; results approximate.

1150. Forbes (*C. N.*, xviii., 275).—Fuse ore with $KHSO_4$, separate SiO_2, and precipitate TiO_2 by boiling much diluted filtrate after acidifying with HNO_3.

1151. Bettel (*C. N.*, xxviii., 93).—As 1150; but omits HNO_3, and adds SO_2 before boiling.

1152. Forbes (*C. N.*, xix., 3).—Decompose powdered mineral with H_2SO_4 or $NaHSO_4$, and proceed as before. The Ti, which goes into solution on dissolving Fe in aqua regia, is all contained in a small precipitate formed with AmHO.

1153. Roussel (*C. N.*, xxviii., 313).—Decompose the mineral with soda. Separate TiO_2 and SiO_2 with concentrated H_2SO_4; Ti from the filtrate with SO_2, &c., and from co-precipitated Al_2O_3 by digesting with HCl (see 1145).

1154. Anon. (*J. I. S. I.*, 1895, i., 514).—Reduce ore in H, dissolve in HCl, fuse residue, dissolve insoluble titanate in HCl, precipitate Fe and Al from tartrate solutions with H_2S, and precipitate TiO_2 by boiling with glacial acetic acid.

1155. Ledebur (*J. I. S. I.*, 1885, 300).—Dissolve ore in HCl, re-treating the insoluble portion; evaporate filtrate with H_2SO_4, partially neutralise, and precipitate by boiling with SO_2. HNO_3 solution of iron evaporated and treated as ore.

1156. Parry and Morgan (*C. N.*, lxvii., 260).—Decompose pig-iron with HCl, fuse ignited residue with $KHSO_4$, and precipitate Ti by boiling. Describe also Riley's process, in which Ti is carried down by a little basic ferric acetate.

1157. Classen (*J. C. S.*, liv., 532).—Precipitate Fe with KHO+H_2O_2 (see 1141), filter, boil off H_2O_2, and precipitate Ti with AmHO. Any Ti carried down with the iron remains suspended when the oxalate solution of the latter is electrolysed.

1158. Brakes (*J. S. C. I.*, 1899, 1097).—Dissolve ore and fusion of the residue in HCl, nearly neutralise, boil with SO_2, remove SiO_2 with HF, and weigh TiO_2.

1159. Baskerville (*J. S. C. I.*, 1900, 419).—Fuse ore with NaF+$KHSO_4$, neutralise HNO_3 solution of the melt, and from faintly HCl solution precipitate TiO_2 by boiling. The estimation of Si, S, P, &c., described.

1160. Hunt, Clapp, and Handy (*C. N.*, lxv., 235).—Decompose Al-Ti alloy with KHO, fuse residue of Fe and Ti with $KHSO_4$, and precipitate TiO_2 by boiling.

1161. Ziegler ((*C. N.*, lxvi., 321).—Fe-Ti alloy fused with $NaHSO_4$, SiO_2 eliminated, and TiO_2 precipitated by boiling. H_2SO_4 driven from the precipitate by igniting with Am_2CO_3.

1162. Jennings (*J. I. S. I.*, 1888, 331).—Decompose ore with HCl, boil with SO_2 and acetic, fuse precipitate and residue, dissolve soda titanate in H_2SO_4, and re-precipitate by boiling.

1163. Austen and Willbur (*C. N.*, xlviii., 113).—TiO_2 can be precipitated from HCl solution of FeO as well as by the usual method if acetic acid be added.

1164. Morgan (*C. N.*, lxxv., 134).—Evaporate acid solution of iron with H_3PO_4, fuse insoluble phosphotitanate successively with K_2CO_3 and $KHSO_4$, and precipitate TiO_2 with acetate.

1165. Levy (*C. N.*, lvi., 209).—The liquid should contain exactly 0·5 per cent free H_2SO_4, and then boiled for six hours. Zn, Cu, Mg, Al, no effect; Fe, results high.

1166. Apjohn (*C. N.*, xxvi., 183).—Decompose rock with $KHSO_4$, precipitate Ti by boiling, and weigh as titanofluoride of potassium.

1167. Drown and Shimer (*C. N.*, xlii., 299).—Heat iron in Cl, absorb Si and Ti in water, evaporate with HCl and H_2SO_4 to separate SiO_2, and precipitate Ti by boiling. Results higher than Riley's process (1156).

1168. Shimer (*C. N.*, lv., 156).—Agreeing determinations of Ti in pig-iron were made—(1) By fusing HCl residue with $KHSO_4$; (2) by dissolving Ti from residue with HNO_3 (see 463), and by 1167. The precipitate formed by boiling always contains P; it is separated by fusion with soda.

1169. Carnot and Goutal (*J. C. S.*, lxxii., ii., 521).—Decompose Fe with neutral cupro-potassic chloride, fuse residue with $KHSO_4$, and precipitate TiO_2 with SO_2 and acetate.

1170. Moissan (*C. N.*, lxxi., 103).—Ti is decomposed by KNO_3 and K_2CO_3, and precipitated with AmHO. Some properties of the metal.

1171. Pennington (*C. N.*, lxxv., 31).—Na_2HPO_4 completely precipitates Ti from its double fluoride solution.

III. Volumetric Estimation of Titanium.

1172. Pisani (*C. N.*, x., 218).—Reduce HCl solution with Zn, and titrate with $KMnO_4$; Zr does not interfere. By using KCNS test, Ti can be titrated in presence of iron, since Ti is first oxidised. H_2S and SO_2 do not reduce Ti. Wiegand (*J. S. C. I.*, 1883, 363).—The estimation in the presence of Fe is unreliable.

1173. Wells and Mitchell (*C. N.*, lxxiii., 123).—Decompose ore with acids and $KHSO_4$, reduce, and titrate H_2SO_4 solution (even in the presence of iron) as 1172.

1174. Weller (*J. S. C. I.*, 1882, 506 and 508).—Mo, V (see 1119), and Cr interfere with the H_2O_2 colour estimation of Ti; NH_3 and K salts, and excesses of the reagent do not appreciably. The yellow colour is due to a higher oxide, TiO_3. (Also Classen, *J. S. C. I.*, 1888, 344).

1175. Dunnington (*C. N.*, lxv., 65).—Evaporate powdered rock with HF, fuse with $KHSO_4$, extract with H_2SO_4, and apply 1174.

1176. Dunnington (*C. N.*, lxiv., 302).—The $KHSO_4$ fusion should be taken up with 5 per cent H_2SO_4 to prevent the formation of meta-titanic acid, which gives no colour with H_2O_2.

1177. Wells (*J. I. S. I.*, 1886, 399).—Dissolve Fe in nitro-sulphuric, evaporate to SO_3, dilute, add H_2O_2, and compare with standard. Will estimate 0·01 per cent Ti.

1178. Noyes (*J. S. C. I.*, 1891, 485).—Open up ore with $KHSO_4$ and NaF, and apply 1174. Very small amounts of Fe interfere, but may be allowed for.

IV. Detection of Titanium.

1179. Riley (*C. N.*, iv., 84).—Treat SiO_2 with HF, fuse residue with Zn and microcosmic salt in order to detect Ti in pig-iron.

1180. Deville (*C. N.*, iv., 241).—Titanate of K in HCl gives with Zn a violet-blue colour. The precipitate formed with AmHO in HCl solution gives a deeper colour when heated with Sn in R.F.

1181. Jackson (*C. N.*, xlvii., 157).—Yellow colour with H_2O_2 in HCl or H_2SO_4 solution; easily detects 1 part in 50,000.

1182. Hillebrand (*C. N.*, lxxii., 158).—HF interferes with H_2O_2 test. H_2O_2 may contain HF.

1183. Fresenius (*C. N.*, lii., 104).—H_2SO_3 which has been momentarily in contact with Zn produces an orange-red colour; about as sensitive as the H_2O_2 test.

1184. Levy (*C. N.*, liv., 301).—Moisten with H_2SO_4, and add morphine; a crimson colour = Ti.

1185. Ludeking (*C. N.*, lxiii., 24).—Fuse in bead of Na_2CO_3 and heat in R.F.; red (cyano-nitride) colour = Ti.

V. Miscellaneous.

1186. Riley (*C. N.*, i., 159).—Analysis of New Zealand iron sands. Ti determined by difference.

1187. Mushet (*C. N.*, i., 231 and 276).—Contention that the "body" and general excellence of certain steels is due to Ti.

1188. Riley (*C. N.*, viii., 224, &c.).—Two or three not very satisfactory processes for estimating Ti (see 1156).

1189. Jones (*C. N.*, lxv., 8).—Refractory Ti minerals containing Al, Mg, Cr, &c., are decomposed by heating with H_2SO_4 in sealed tube.

1190. Blondel (*C. N.*, lxxix., 305).—Beyond 200°, H_2SO_4 solutions of TiO_2 deposit crystals which stop the decomposition of the mineral. TiO_2 slowly precipitated at ordinary temperatures.

1191. Hogg (*C. N.*, lxviii., 163).—As isolated crystals of cyano-nitride Ti exists in ferro-manganese.

1192. Hillebrand (*C. N.*, lxxviii., 94).—Description of H_2O_2 colour test. Zr prevents precipitation of TiO_2 by boiling acetic solutions. Separates Fe and Al from Ti as 1139.

1193. Nau (*J. I. S. I.*, 1892, ii., 437).—Ti may not be detectable in pig-iron even when the slag contains 8 per cent or more TiO_2.

1194. Reinhardt (*J. S. C. I.*, 1888, 326).—Separation of cyano-nitride (Ti_5CN_4) from slags, and analysis thereof. (Also Franck, *J. S. C. I.*, 1897, 942).

(END OF PART VIII.).

A METHOD FOR PREPARING NORMAL, SEMINORMAL, DECINORMAL, &c., SULPHURIC ACID OF EXACT STRENGTH.*

By RICHARD K. MEADE.

The principal beauty of the normal system in volumetric analysis is the doing away with calculations. If then it is necessary to use a factor for converting to normal with a solution much of the usefulness of the system is destroyed. Unfortunately with by far the larger number of reagents used in volumetric analysis it is only with the greatest care that such solutions can be made of normal strength. Of the commonly used acid and alkali solutions, only oxalic acid and sodium carbonate can be prepared of exact strength, without first having another standard solution against which to balance a preliminary and then the exact solution. Even then, the latter is frequently too wide of the normal value to be used without a factor. The writer has been for some time preparing normal, seminormal, and more particularly decinormal sulphuric acid of exact strength by the method given below. The solution as prepared by this method needs no checking, except as a safeguard against errors of manipulation on the part of the analyst.

If the electric current is passed through a solution of copper sulphate the salt is decomposed, copper separating upon the cathode and sulphuric acid at the anode. This latter remains in solution and is not decomposed by the current. Hart and Croasdale (*Journ. Anal. Chem.*, iv., 424) took advantage of this reaction to standardise alkali solutions. Their results were highly accurate. The writer has frequently made use of this method of standardising alkali and has obtained results far more satisfactory than by any other method.

The method of preparing tenth-normal sulphuric acid by means of this reaction is as follows:—

12·487 grms. of pure crystallised copper sulphate are dissolved in about 750 c.c. of distilled water in a lipped beaker capable of holding about a litre. Into this solution, after cooling, is introduced a cylinder of copper foil attached to the minus (−) wire of an electric circuit. This copper cylinder may be made from 0·015 inch copper foil. The foil is cut the required length (three times the diameter of the beaker + one-half inch), curled so that the ends lap, and holes punched through the two thicknesses of foil with a sharp nail. Wire is then run through the holes, fastening the two ends of the foil together. A platinum rod for an anode is next passed through a perforated watch-glass covering the beaker into the copper sulphate solution. A current of electricity of from one to one and a-half ampères is now passed through the solution for about eight hours; or all night if the decomposition is

* Contribution from the Chemical Laboratory of Lafayette College. From the *Journal of the American Chemical Society*, xxiii., No. 1.

begun in the afternoon. In the morning the watch-glass is removed and rinsed off together with the cylinder and the rod into the beaker. The solution is then transferred to a litre graduated flask; any copper which may have dropped off the cylinder into the beaker is to be washed well by decantation, rinsing the beaker at the same time into the flask. The contents of the latter are then diluted to the mark.

The first few solutions made in this way were subjected to the following tests:—

A portion of the solution was carefully evaporated to small bulk and hydrogen sulphide passed into the liquid. No precipitate formed.

Another portion of the solution was evaporated to a few cubic centimetres, ammonia added, and the test-tube stood upon white paper. No blue colour.

A third portion of the solution, after evaporation, was placed in a bright platinum dish, a drop of nitric acid added, and a weak current passed through the solution. After one hour no copper stain appeared on the dish and the platinum was still bright.

The results given by the first solution made, when checked by volumetric and gravimetric methods, are given below:—

An exactly tenth-normal solution of sodium carbonate, made by igniting pure bicarbonate and then dissolving 5·305 grms. of the resulting sodium carbonate in a litre of water, was first used.

Check No.	Sodium carbonate solution taken.	Sulphuric acid solution required to neutralise.
	C.c.	C.c.
1	25·0	25·0
2	25·0	25·1
3	15·0	15·05
4	15·0	14·9

A tenth-normal sodium hydroxide solution was next used. This solution was made by dissolving freshly cut clean bright pieces of metallic sodium in water contained in a silver dish and covered with a large inverted funnel. It was preserved in a large bottle, and drawn off for use by means of a syphon passing through the stopper of the bottle. All air entering the bottle passed through a soda-lime tube, capped when not in use. This sodium hydroxide solution had been checked against a fifth normal hydrochloric acid solution, which in its turn had been standardised by precipitation with silver nitrate. It was also checked by the copper sulphate and battery method of Hart and Croasdale. These checks established a factor, 0·99501, for converting to tenth-normal.

Check No.	Sodium hydroxide solution taken.		Equivalent volume of N/10 solution.	Sulphuric acid solution required.
	C.c.		C.c.	C.c.
1..	10	× 0·995 =	9·95	10·0
2..	10	× 0·995 =	9·95	9·9
3..	20	× 0·995 =	19·9	19·9

Finally, 25 c.c. of the sulphuric acid solution were acidified with a few drops of hydrochloric acid, heated to boiling, and an excess of a hot 10 per cent solution of barium chloride slowly added with constant stirring. After standing all night, the precipitate was filtered off, ignited, and weighed.

1. Weight of barium sulphate .. 0·2923 grm.

The molecular weight of barium sulphate is 233·46; hence, 25 c.c. of a tenth-normal solution should give—

$$\frac{233{\cdot}46 \times 25}{2 \times 10 \times 1000} = 0{\cdot}29183 \text{ grm. barium sulphate.}$$

The solution is therefore a little under tenth normal, or 2923 : 2918 :: x : 1; x = 1·002, which gives the factor for converting to tenth-normal.

2. Weight of barium sulphate ..	0·2938 grm.
Factor is in this case	1·003
Average factor for the two determinations	1·0025

Of course, the results by precipitation with barium sulphate would be worthless if the absence of copper had not been previously proved.

Since making this solution, the writer has repeatedly made normal and fifth-normal solutions by this method; it was not until recently though, that he had occasion to make a normal solution. In this case, 124·87 grms. of copper sulphate were dissolved in 800 c.c. of water and decomposed by a current of 2·5 ampères. The decomposition was complete in about twelve hours, though the current was allowed to run nearly eighteen. After making up to a litre, the strength of the solution was taken against the sodium carbonate solution mentioned above, with the following results:—

Sulphuric acid solution taken.	Sodium carbonate solution required.
C.c.	C.c.
5·0	50·1
5·0	50·2
5·0	49·8
5·0	49·95
Average	50·025

100 c.c. of the normal solution were then diluted to 1000 c.c. in a graduated flask, and, after mixing, tested against the N/10 sodium hydroxide solution mentioned above.

Sodium hydroxide solution taken.			Equivalent volume of N/10 alkali solution.	Sulphuric acid. required.
C.c.			C.c.	C.c.
10·0	× 0·995	=	9·95	10·1
10·0	× 0·995	=	9·95	10·0
10·0	× 0·995	=	9·95	10·0
10·0	× 0·999	=	9·95	9·95
10·0	× 0·995	=	9·95	9·95
Average				10·00

All of the solutions made by this method have been checked against the sodium hydroxide solution, with the result that the strength of the sulphuric acid solution is always the desired one.

THE MINERAL CONSTITUENTS OF DUST AND SOOT FROM VARIOUS SOURCES.*

By W. N. HARTLEY, F.R.S., Royal College of Science, Dublin, and HUGH RAMAGE, A.R.C.Sc.I., St. John's College, Cambridge.

(Concluded from p. 159).

On the Nature of Dust from the Clouds.

The principal characteristic of dust which has fallen directly from the clouds or collected by hail, snow, sleet, or rain, is its regularity in composition—each specimen appears to contain the same proportions of iron, nickel, calcium, copper, potassium, and sodium. The proportion of carbonaceous matter must be small, otherwise a diminution in the proportion of the metals present would render the metallic lines weaker. There is a very considerable difference between the dust from sleet, snow, and hail suddenly precipitated, the difference being in the proportion of lead, which, in the dust from sleet, is much larger than in the other specimens, though dust from hail and one quantity collected from rain contain more than is found in any other specimens with such an origin. The only meteorite which contains as much lead as this is the siderolite from Atacama.

Of Volcanic Dust.

If we examine the spectra of specimens of volcanic dust it is noticeable that the heavy metals are, without excep-

* A Paper read before the Royal Society, February 21, 1901.

THE LINES OF IRON OBSERVED IN DIFFERENT KINDS OF SOOT.

	Laundry.	Laboratory.	Kitchen.	Bedroom.	
Na D	5893·0				
	4404·9				
	4383·7	4383·7			
	25·9				
G	08·0				
	4289·8				
	16·3	4216·0			The two rubidium lines 4215·8 and 4202·4 almost coincide with two iron lines 4216·3 and 4202·1.
	02·1				
	4144·0	4144·0			
	32·2				
	4063·7				
	45·9				
	3930·4	3930·4		3930·4	
	28·0	28·0		28·0	
	23·0	23·0		23·0	
	20·4	20·4		20·4	
	06·6	06·6		06·6	
	3899·9	3899·9		3899·9	
	95·8	95·8		95·8	
	86·4	86·4	3886·4	86·4	
	78·7	78·7	Extremely feeble.	78·7	
	72·6	72·6			
	65·6				
	60·0	60·0	3860·0	3860·0	
	56·5	56·5	Very feeble.	56·5	
	50·1	50·1			
	40·5	40·5			
	34·3	34·3			
	26·0	26·0		3826·0	
L	24·5	24·5	3824·5	24·5	
	20·5	20·5	Barely visible.	20·5	
	15·9	15·9			
	13·1	13·1			
	3799·6	3799·6			
	98·6	98·6			
	95·1				
	88·0	88·0			
	49·6	49·6	3749·6	3749·6	
	45·7	45·7	45·7	45·7	
	35·0	35·0	35·0	35·0	
	33·4	33·4	33·4	33·4	
M	27·7	27·7			
	22·6	22·6	3722·6	3722·6	
	20·0	20·0	20·0	20·0	
	09·3	09·3	The six last lines	09·3	
	05·7	05·7	are very feeble.	05·7	
	3687·6	3687·6		3687·6	
	80·0	80·0			
	77·8	77·8		3677·8	
	47·9	47·9			
	31·6	31·6			
	18·9	18·9			
N	3585·5	3585·5			
	81·3	81·3			
	70·2	70·2			

tion, in comparatively small proportions—lead and iron, for example—while lime, magnesia, and the alkalis are the chief basic constituents. The spectra of the heavy metals, the alkaline earths, and the magnesia with the alkalis appear on separate photographs.

Of Soot from different Chimneys.

The nature of soot from different sources is characterised by the small proportion of iron in most specimens and of metals precipitated as hydroxides; its large proportion of lime, and the greater variability in the proportions of its different constituents distinguishes it from other kinds of dust collected from the clouds or in the open air. It was certainly unexpected when nickel, calcium, manganese, copper, and silver were found to be constant constituents of soot fron different chimneys and flues. The proportions of lead, silver, and copper are much larger in the soot from the assaying furnace and the laundry chimney.

To illustrate the differences observable in dust and soot of various kinds, a list is appended of the wave-lengths of the iron lines observed in the spectra from soot obtained from the laundry, laboratory, kitchen, and bedroom chimneys. A second list gives the wave-lengths of lines belonging to other elements, and observed in other substances as well as dust and soot.

It will be seen that there is an extraordinary difference between the kitchen and the laundry soot, which is probably caused by a higher temperature and more complete combustion of the fuel in the laundry fire.

Flue Dust.

In flue dust from different sources the chief character-

Wave-lengths of other Lines than Iron in Spectra from various kinds of Dust and Soot, and in Meteorites.

Sodium.

D lines. 5896·1, 5890·2 } Mean 5893·0
3303·1, 3302·5 } Mean 3302·3

Potassium.

5805·0
4047·4, 4044·0 } Mean 4045·7

Lithium.

4602·3
3232·7

Cæsium.

4557·0

Rubidium.

4215·7
4202·4

Thallium.

5349·6
3775·6

Gallium.

4172·2
4033·0

Indium.

4511·0
4102·0

Calcium.

4226·9 A line.

Calcium Oxide.

5598·0 to 5485·0 } A strong band.
6253·0 to 6116 0 } A band.
6075·0 to about 5985 0 } A weaker band.

Magnesium Oxide.

3929·0 to 3856·0 } A band, strong, diffuse.
3834·0 to about 3805·0 } A band, strong, diffuse.

Strontium.

4607·0

Lead.

4057·6
3682·9
3639·2

Chromium.

4289·9, 4274 6, 4254·4 } A triplet.
3605·3, 3593·7, 3578·8 } A triplet.

Manganese.

4034·5, 4033·2, 4031·0 } Lines which often appear like one broad line.

Copper.

3273·6
3247·0

Silver.

3383·5
3282·1

Nickel.

3618·5, 3609·8, 3571·2, 3461·0, 3433·0 The lines observed are near the positions of such as are here indicated, and are probably identical with them. There is also a line 3525, the only one observed in Cleveland pig-iron. It does not appear in these analyses.

Some of the lines were measured with a micrometer and the wave-lengths deduced from a curve on an enlarged scale drawn from Rowland's measurements of iron lines in the solar spectrum.

istics are the presence of lead, silver, and copper in larger proportions than in other varieties of dust or of coal ashes which have also been examined. Nickel and manganese also are in larger proportions. But the most striking feature is the quantity of rubidium, gallium, indium, and thallium in all samples examined.

It is evident now that we can state with absolute certainty whether two kinds of dust have the same composition, or in what constituents they differ substantially.

When dust is collected in the open air it is liable to become mixed with other dust and soot, and we cannot be certain whether it comes from only one source or not, but soot, as a rule, can be separated by washing it away from the heavier matter. The occurrence of nickel in soot and flue dust was certainly unexpected. It is probably disseminated in extremely minute traces in coal, and its concentration in soot is owing to the conditions in a coal fire being favourable to the formation of nickel tetra-carbonyl and its subsequent decomposition.

Conclusions.

(1). The presence of nickel, as shown by the examination of soot, is not positive evidence that the dust from the clouds comes from other than a terrestrial source.

(2). The dust which fell on the 16th and 17th of November, 1897, with its regularity in composition and its similarity to meteorites, being magnetic, also its comparative freedom from extraneous matter, exhibits properties which are quite in favour of its cosmic origin. Moreover, its composition is totally unlike that of volcanic dust and flue dust from various chemical and metallurgical works. This dust for the most part fell on a perfectly calm fine night, and there was no rain for twenty-four hours or more afterwards.

We beg to draw attention once more to the very wide distribution of gallium in minute proportions; it occurs in all aluminous minerals, flue dust of very different kinds, soot and atmospheric dust, also in a great variety of iron ores. Bauxite contains it in larger proportion than any other mineral, but the quantity even in this substance is very small. We have hopes of finding it concentrated in some mineral, as thallium, cæsium, germanium, and indium are. Indium and thallium, the other members of the same group of elements, are found in blende and pyrites, and accordingly we might expect gallium to occur in a concentrated state in a sulphide, arsenide, or similar compound. Judging, however, from its analogy with aluminium, there does not seem to be much probability of this.

SOME PRINCIPLES AND METHODS OF ROCK ANALYSIS.*

By W. F. HILLEBRAND.

(Continued from p. 166).

XI. *Magnesium.*

Precipitation.

The first precipitation of magnesium is made without special precautions in the filtrate from the first calcium oxalate separation (p. 165), by sodium-ammonium-hydrogen phosphate (microcosmic salt)† in indefinite decided excess, and without the great excess of ammonia usually prescribed. It is not necessary to first remove ammoniacal salts unless very little magnesium is present, and then only in order to hasten precipitation. Neubauer (*Zeit. fur Angew. Chemie*, 1896, p. 435), has shown that precipitation is complete even in presence of large quantities of salts of ammonium, including the oxalate.

* *Bulletin of the United States Geological Survey*, No. 176.

† The objection that has been made by one writer to the use of this salt instead of disodium-hydrogen phosphate is, so far as our experience teaches, entirely groundless.

He has, however, also shown that the composition of the precipitate is largely affected by ammonium salts, and also by the way in which the precipitation is made. These points are only of importance when a single precipitation is to be made or in the final of two or more, as will be discussed later.

Platinum sulphide usually strongly contaminates the separated phosphate, but this matters not, as it remains on the filter when the phosphate is re-dissolved in hydrochloric acid, of which not more than the amount really needed should be used. The solution thus obtained is united with that of the residue from evaporation and ignition of the second filtrate from calcium oxalate, and is diluted if necessary. A few drops of sodium-ammonium phosphate solution are now added, and ammonia in slight excess, with constant stirring till the crystalline precipitate has well formed. The large excess of ammonia of 0·96 specific gravity (one-third the original volume), usually prescribed has been shown by Gooch and Austin (*Amer. Journ. Sci.*, 1899, Fourth Series, vol. vii., p. 187; Chemical News, 1899, vol. lxxix., pp. 233 *et seq.*; *Zeit. fur Anorg. Chemie*, 1899, vol. xx., p. 121), to be quite unnecessary, in fact disadvantageous.

Neubauer in the above-cited paper has shown, and Gooch and Austin (*loc. cit.*) have confirmed his statements, that it is only by working under these conditions —absence of any large excess of precipitant, of ammoniacal salts, and of ammonia—that a precipitate of normal composition is obtainable. It usually differs from the normal in containing relatively more ammonium and less magnesium—for instance, an admixture of such a molecule as $Mg(NH_4)_4(PO_4)_2$—the result being that when ignited in the ordinary way too much magnesium is found, because of formation of some metaphosphate. To obviate this error Neubauer considers it absolutely necessary to blast the precipitate for half-an-hour, and then to repeat the blasting for a second half-hour to see if a constant weight has been reached. The phosphate is then entirely pyrophosphate, which is quite unaffected by further blasting. The intense heat has caused a decomposition of the metaphosphate with volatilisation of P_2O_5, as follows:— $2Mg(PO_3)_2 = Mg_2P_2O_7 + P_2O_5$. Neubauer worked with the usual excess of ammonia, and it remains to be seen whether by precipitating and working according to Gooch and Austin the composition of the precipitate is always close enough to the ideal $MgNH_4PO_4$ to obviate the necessity for blasting.

From the labours of Neubauer and of Gooch and Austin it is clear that the common way of adding the phosphate precipitant to the ammoniacal solution of the magnesium salt is not calculated to produce a precipitate of normal composition. The precipitant should be added to the acid solution of the magnesium, and ammonia should then be added in slight excess.

Gooch and Austin call attention to a modification proposed some years ago by Wolcott Gibbs (*Amer. Journ. Sci.*, 1873, Third Series, vol. v., p. 114), whereby the phosphorus and magnesium salts are first boiled together in neutral solution for a few minutes, and to the cooled solution ammonia is added. The results are said to be remarkably exact.

Methods of Collecting and Igniting the Precipitate.

If the blast has not to be employed, the weight of the pyrophosphate can doubtless be most accurately arrived at by collecting and igniting the precipitate in a Gooch crucible, provided the asbestos felt is well constructed, and not of the serpentine variety so largely on the market.

Neubauer ignites slowly in platinum after drying, without removing from the paper, applying the blast only when the carbon has been wholly burned off (*Zeit. fur Anal. Chemie*, 1894, vol. xxxiii., p. 362; *Journ. Amer. Chem. Soc.*, 1894, xvi., p. 289).

Almost as exact are the two modifications of the method in use for phosphate analyses at the agricultural experiment stations at Danzig and Lisbon, described by Schmoeger (*Zeit. fur Anal. Chemie*, 1898, xxxvii., p. 308), and Mastbaum (*Zeit. fur Anal. Chemie*, 1898, xxxvii., p. 581). According to the former the precipitate after drying is detached from the paper and placed in a platinum crucible, followed by the folded filter. To the covered crucible the full flame of a burner is applied, and after a short time the burning off of the carbon is accomplished with the crucible open. A short blasting follows. In a number of experiments on quantities ranging from 0·06 to 0·28 grm. of pyrophosphate the results were, with a few exceptions, naturally lower than those obtained on duplicates by the ordinary method of igniting, but only by 0·0013 grm. in maximum.

Mastbaum, to shorten time, applies the full flame to the moist precipitate wrapped in its filter. Later, when most of the carbon is burned off, he moistens the residue with two or three drops of strong nitric acid, evaporates this carefully, heats with full burner for a few minutes, then blasts for half a minute. He describes the results as irreproachable. In this laboratory only the Mastbaum modification has been tried, and it certainly seems to be satisfactory when the extreme of accuracy is not required.

At one time the procedure first recommended by Ulbricht, later by Broockmann, and also by L. L. de Koninck, was used. It consists in dissolving the ammonium-magnesium phosphate off the filter with nitric acid, collecting the filtrate in a weighed crucible, evaporating the contents to dryness,* and subsequently igniting, the product being presumably pyrophosphate. But it was soon observed that the ignited salt, especially when large in amount, does not always dissolve completely in hydrochloric acid, but that sometimes a white residue is left in light lumps which appears to be quite insoluble in acids. This residue contains no silica, but only the constituents of a magnesium phosphate, and it may be a peculiar metaphosphate. Whether its appearance is due to an abnormal composition of the original magnesian precipitate or to conceivable change during evaporation in the crucible with nitric acid remains to be determined. Until this is done the employment of this method of igniting is not to be recommended.

Contamination by and Removal of Barium and Calcium.

Barium phosphate will not contaminate the second magnesian precipitate unless there are notable amounts of barium in the rock, in which case it must be removed by sulphuric acid prior to the final precipitation of the magnesium. Calcium, however, is probably never absent, and has to be estimated and allowed for as follows:—

To the ignited pyrophosphate, dissolved in but slight excess of hydrochloric acid, is added ammonia to alkalinity, and then acetic acid, drop by drop, till the solution, which should not be hot, clears. It now and then happens that a little flocculent matter fails to dissolve. This is to be removed, ignited, and subtracted from the original weight. It is likely to consist, in great part or wholly, of phosphates of iron or manganese, or both, and shows often a reddish colour on ignition. If an excess of acetic acid has been used, this is cautiously removed by ammonia. Then a drop or two of solution of ammonium oxalate is added, and the small beaker is set aside for twelve hours if necessary. Almost invariably a small precipitate soon shows itself, which if fine-grained and non-adherent to the glass may be regarded as pure calcium oxalate; otherwise it contains, or may largely consist of, magnesium oxalate. It is in that case to be collected, ignited, re-dissolved, and re-precipitated. Its final weight, averaging perhaps one-half milligrm., is to be added to that of the lime already found, and subtracted as tricalcium phosphate from that of the magnesium pyrophosphate in order to arrive at the true figure for magnesia. This separation, to be satisfactory, requires great care.

* A pink colour of varying intensity almost invariably becomes apparent as the mass approaches dryness, a most delicate test for the traces of manganese which always escape precipitation by ammonium sulphide or bromine.

XII. *Titanium.*

Colorimetric Estimation with Hydrogen Peroxide, Weller's Method (*Ber. Deutsch. Chem. Gesell.*, 1882, xv., p. 2593).

The method consists in comparing the colour of a known bulk of solution to be tested with that of a standard solution of titanium sulphate, both having been fully oxidised by hydrogen peroxide. The strength of the peroxide should be approximately measured by titration with permanganate on opening a fresh bottle, and again after a few weeks, otherwise very serious error may arise through its deterioration.

Mere traces of hydrofluoric acid, either in the peroxide or the titanium solution, render this method inexact (Hillebrand, *Journ. Amer. Chem. Soc.*, 1895, xvii., p. 718; Chemical News, 1895, lxxii., p. 158; *Bull. U.S. Geol. Survey*, No. 167, p. 56), hence care should be exercised as to the character of the peroxide, which, as sold in the market, often contains fluorine.

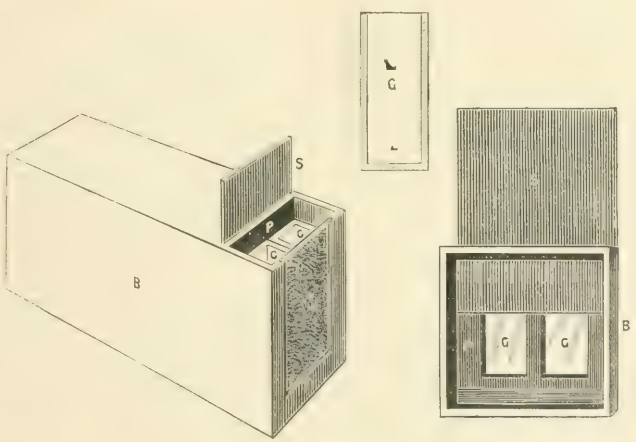

Fig. 12.—Apparatus for Colorimetric Determinations in Different Aspects.

G, One of two glasses of square or rectangular section, 8 to 12 c.m. high and 3 to 3½ c.m. inside measurement between those sides through which the liquid is to be observed; the other sides are blackened on the outside. B, Rectangular box, about 35 c.m. long and 12 c.m. square, stained black inside and out, one end closed by a ground-glass window, W, the other open, and a portion of the top removed. P, Blackened partition, with openings corresponding to the interior dimensions of the glasses when in position. S, Blackened cardboard shutter sliding stiffly up and down between partition and glasses, so as to shut off all light above the lowest surface of the liquid in the glasses

Dunnington (*Journ. Amer. Chem. Soc.*, 1891, xiii., p. 210), has pointed out the necessity for the presence of at least 5 per cent of sulphuric acid in solutions which are to be thus tested for titanium, in order, as he concludes, to prevent partial reversion to metatitanic acid which does not give a colour with hydrogen peroxide. The standard solution of titanium sulphate, holding conveniently about 1 centigrm. TiO_2 in 10 c.m.^{3}, equivalent to 1 per cent of TiO_2 in 1 grm. of rock, contains therefore 5 per cent or more of sulphuric acid. Of this 10 c.m.^{3} are mixed with a sufficiency of hydrogen peroxide (2 c.m.^{3} of most commercial brands is ample), and diluted to 100 c.m.^{3} in a measuring flask.

Titanium can be estimated, as a rule, most conveniently in the solution which has served for the titration of total iron (p. 150). This, having been evaporated, if necessary, to less than 100 c.m.^{3}, is to be fully oxidised with hydrogen peroxide, and if the colour is less intense than that of the standard, is made up to 100 c.m.^{3} with dilute sulphuric acid in a measuring flask, and mixed; otherwise, in a flask of sufficient size to insure that its colour shall be less intense. One of the rectangular glasses described below being filled with the solution to be tested, 10 c.m.^{3} of the diluted standard are run into the other from a burette, and water is added from a second burette until there is no distinction as to colour. A second and a third portion of the standard can be run in and diluted, and the mean of several determinations struck, when a simple calculation gives the percentage of TiO_2 in the rock.

If the convenient but expensive Soleil-Duboscq colorimeter is used, or the simple Nessler tubes, it is of course unnecessary to dilute the rock solution to the extent above required, should it be stronger than the standard. Experience has shown, however, that differences can not be sharply estimated in strongly coloured solutions, and that the results are much more satisfactory when the colour intensity is not much, if any, greater than that given by a standard of the above concentration. For the percentages of titanium found in rocks, clays, and soils, usually under 1 per cent, but rising to 2 or even 3 per cent or more occasionally, the colorimeter method gives results which are fully equal to those of the best gravimetric method, besides being a great time saver. The error introduced by iron, in consequence of the yellowish colour of its sulphate solution, is practically negligible unless its percentage is very high; then either the iron must be removed prior to making the colour test, or correction should be applied for known amounts of ferric sulphate in solutions of the requisite dilution.

The exact correction to be applied in such cases is difficult of determination because of the impossibility of matching the colours of titanium peroxide solutions with those of ferric sulphate; but tests made go to show that the colouring effect of 0·1 grm. of Fe_2O_3 in 100 c.m.^{3} 5 per cent sulphuric acid solution is about equal to 0·2 milligrm. of TiO_2 in 100 c.m.^{3} when oxidised by hydrogen

peroxide. This amounts to a correction of only 0·02 per cent on 1 grm. of rock containing the unusual amount of 10 per cent Fe_2O_3. It will be more satisfactory, when much iron is present, to remove this as described hereafter, and to colorimetrically estimate the titanium thus freed from iron.

Alternative Mode of Preparing the Test Solution.

As said above (pp. 150 and 177), the solution that has been used for volumetric estimation of total iron can most conveniently be used for the colorimetric determination of titanium, but if desired this can, of course, be made on some other portion of rock powder. At one time it was the practice in this laboratory to combine it with the determination of barium, as described in *Bulletin* 148 *of the United States Geological Survey*, by decomposing the powder by sulphuric and hydrofluoric acids,* expelling the latter by repeated evaporations with sulphuric acid, taking up with dilute sulphuric acid,† filtering from barium sulphate, &c., and estimating the titanium colorimetrically in the filtrate. The expulsion of fluorine must be thorough, or else the titanium result will be low, as already stated (p. 177), and it is not always easy to effect this complete removal, though the time required to do so seems to be in no slight degree dependent on the nature of the fluorides to be decomposed. Long after every trace of fluorine seems to be gone, the formation of a crust on the evaporating solution sometimes allows an accumulation of enough hydrofluoric acid gas to become plainly manifest to the smell on breaking the crust.

The Colorimetric Apparatus and its Use.

The glasses G (Fig 12) may be of square or rectangular section, 8 to 12 c.m. high, and 3 to 3½ c.m. inside measurement between those sides through which the liquid is to be observed.‡ These sides should, of course, be exactly parallel; the others need not be, but should be blackened externally. In order to further exclude the effect of side light in this and other similar methods (chromium, for instance, see *prox.*), it is very convenient to have a simple light box (B, Fig 12) that can be easily held in one hand about 35 c.m. long and 12 c.m. square, stained black inside and out, and with one end closed by a piece of ground glass, W, the other open. For a space equal to the width of the glasses the cover is removed at the top next the glass end to permit of the insertion of the glasses side by side in such a way that no light shall penetrate around their sides or between them. Immediately back of the glasses is a partition, P, with openings of appropriate size cut in it. A stiffly sliding black cardboard shutter, S, is movable up and down immediately back of the partition, so that all light can be cut off except that which comes through the liquid.

Precautions of this kind are necessary if accurate results are to be counted on. Except for mere traces, this combination of glasses and darkened box insures greater accuracy and rapidity of work than Nessler tubes, and is preferable likewise, so far as the writer's experience goes, to expensive instruments like the colorimeter of Soleil-Duboscq, &c. In making the colour comparisons the box is best held close to a window, so as to get a full, strong light. Daylight is far preferable to artificial light.

(To be continued).

* It is to be borne in mind that evaporation with hydrofluoric acid alone results in loss of titanium by volatilisation, but that there is no loss if excess of sulphuric acid is also present.

† With acid rocks solution is very complete, and it can be made nearly so with the most basic by transference to a small beaker, and gentle boiling. The residue thus obtained may contain, besides barium sulphate, a little calcium sulphate, zircon, andalusite, topaz, and possibly a trace of titanium in some form. It is therefore to be thoroughly fused with sodium carbonate, leached with water, fused with potassium bisulphate, dissolved in dilute sulphuric acid, filtered, and the filtrate added to the main one. The insoluble matter will now be chiefly barium sulphate, for the further treatment of which see *prox.*

‡ The allowable error in distance between the corresponding pairs of sides of the two glasses should not in any case exceed 1 per cent. Unfortunately there seems to be a disinclination or inability on the part of dealers in this country to furnish glasses fulfilling this requirement, and held together by a durable cement which shall be proof against dilute sulphuric acid. Canada balsam answers well for a time, but sooner or later it cracks, leaks then appear, and the sides soon drop off. It is, however, but a simple matter to cement them on again. A pair of entirely satisfactory glasses can be made from a couple of square or rectangular 3 to 4 ounce bottles by cutting off one pair of sides from each, and grinding down till the calipers show that agreement is perfect. The tops are then to be sawed off and pieces of plate glass cemented on the sides.

NOTICES OF BOOKS.

The Theory of Ions and Electrolysis (La théorie des ions et l'électrolyse). By Auguste Hollard. Paris: Georges Carré and C. Naud. 1900. Pp. 159.

Of late years electrolysis has been the subject of a large amount of work, both from the theoretical and the practical point of view. Chemistry has been enriched by new methods for the separation and estimation of the elements, while in metallurgy the progress have been so great that practically new industries have been created.

Unfortunately, in electrochemistry the purely scientific researches on the one hand, and the purely practical ones on the other, have too often been carried out with absolute independence; up to quite recent times the practical man has wasted a great deal of time and money by not being acquainted with the facts which have been discovered by his scientific brother. Now, however, the books which have been written on electrochemical science have given to the world a number of new facts, and on these facts the *theory* of electrochemistry has been built up, by means of which not only that which is known can be explained, but even the unknown can be foretold to a certain extent.

The author, who is well-known in connection with this subject, gives in this volume a full and clear account of the present views held on the theory of ions applied to electrolysis; he, however, deals mostly with electrolytic phenomena in aqueous solutions when using continuous currents, and more particularly with the electrolysis of metallic salts.

The phenomena examined may be summarised as follows:—The manifestations of electric energy in the electrolyte: this energy may be looked upon as the product of two factors, *quantity* and *tension*; the author prefers this latter expression to the older form, "difference of potential."

This leads to the examination of the constitution of electrolytes, their conductibility, and, finally, the electric *tension* and the *work* necessary to effect the electrolysis. The book is well printed and bound, and makes a far more handsome and durable volume than we are accustomed to receive from French publishers.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxii., No. 11, March 18, 1901.

Action of Acids on the Carbonates of the Alkaline Earths in presence of Alcohol.—C. Vallée.—M. Carette found that hydrochloric and nitric acids attack calcium carbonate in presence of absolute alcohol, sulphuric acid attacks it but slightly, and certain organic acids, such as acetic, have no action at all. The author substitutes for ethyl alcohol acetone and methyl alcohol, and finds that apparently there is no difference in the behaviour of the

acids. He further investigates the action of sulphuric acid, by adding normal sulphuric acid to absolute alcohol and placing the mixture in presence of excess of chalk. Titrations taken from time to time show that four months is necessary for the neutralisation to be complete, even when the mass is frequently agitated. Such an experiment shows that the reaction is simply very slow and is not limited.

Compounds of Cæsium.—C. Chabrié.—Cæsium was the first of the metals discovered by means of spectrum analysis (1861). It has not been very much examined owing to its rarity. The author obtains the metal from Pollux and from this prepares a number of cæsium compounds—the bromide, CsBr, the iodide, CsI, in the form of white cubic crystals, the fluoride, CsF.HF, in long hygrometric needles, neutral cæsium chromate, CrO_4Cs_2, and cæsium bichromate, $Cr_2O_7Cs_2$.

Constituents of Industrial Ferrosilicons.—P. Lebeau.—The author's investigations on the compounds of iron and silicon definitely establish the existence of the silicides, $SiFe_2$, SiFe, and Si_2Fe, in industrial ferrosilicons. He prepares all these compounds in a pure crystalline form and makes a study of their principal properties. The results obtained facilitate researches concerning the structure of silicated alloys. Finally, the siliciuration of iron by electro-metallurgical methods can have two limits, corresponding to the formation of the compounds SiFe and Si_2Fe, according to the nature of the original materials used.

Action of the Chlorides of Acids and the Anhydrides of Acids on the Organo-metallic Compounds of Magnesium.—MM. Tissier and Grignard.—In a former paper M. Grignard explained the importance of the organo-metallic compounds of magnesium for syntheses in organic chemistry. The authors now apply these substances for the study of the chlorides and anhydrides of certain organic acids.

Action of Caprylic Alcohol on its Sodium Derivative. Synthesis of Dicaprylic and Tricaprylic Alcohols.—Marcel Guerbet.—The author continues a former research on the action of the primary alcohols of high atomic weight on their sodium derivatives. He now extends his researches to the secondary alcohols, taking as an example caprylic alcohol, $C_8H_{18}O$. By the action of this alcohol on its sodium derivative dicaprylic alcohol, $C_{16}H_{34}O$, and tricaprylic alcohol, $C_{24}H_{50}O$, are obtained, the reactions apparently taking place according to the equations—

$$C_8H_{18}O + C_8H_{17}NaO = C_{16}H_{34}O + NaOH.$$
$$C_{16}H_{34}O + C_8H_{17}NaO = C_{24}H_{50}O + NaOH.$$

Vaporisation and Hydratation of Ethylenic Glycol.—M. de Forcrand.—The author finds the boiling-point of glycol under varied pressures, from which the curve of vapour tensions can be constructed. He notices also that glycol is extremely hygroscopic, absorbing water vapour from the air in the same way as sulphuric acid or absolute alcohol, and he determines a number of heats of solution.

Dissociation and Thermic Examination of the Compound $Al_2Cl_6.18NH_3$.—E. Baud.—When a current of ammonia gas is passed over dodecammoniacal aluminium chloride cooled to 0°, no increase in weight is observed. The same is the case at a temperature of −10·7°, but if the whole is cooled down to −18° or −20° a body is obtained having the composition $Al_2Cl_6 + 16·43NH_3$. At −22° or −23° the compound becomes $Al_2Cl_6 + 17·7NH_3$. A new substance is evidently produced having for its probable formula $Al_2Cl_6.18NH_3$ and whose dissociation tension is equal to atmospheric pressure between −10·7° and −18°.

Direct Nitration in the Fatty Series.—A. Wahl.—The author examines the action of fuming nitric acid on the non-saturated compounds, and afterwards on the other derived ethers of ethyl acrylate, such as ethyl crotonate, ethyl tiglate, and ethyl isolauronolate.

The Pretended Bi-naphthylene Alcohol.—R. Fosse.—The author's researches show that the pretended bi-naphthylene of Rousseau appears to be, in reality, nothing else but a derivative of tri-naphthyl methane.

Ethyl-β,β-Diacetylpropionate.—F. March.—In a former paper the author announced the preparation of ethyl-ββ-diacetyl propionate—

$$(CH_3—CO)_2—CH—CH_2—COOC_2H_5$$

and its action on phenylhydrazine. He now prepares certain derivatives of this compound and also the barium, potassium, sodium, copper, and silver salts.

Properties of the Alcoyl Substitution Products of Acetone Dicarbonate of Monocyano-ethyl. Action of Cyanogen Chloride on Methyl Acetone Dicarbonate.—J. Derôme.

Action of Butyryl Chloride on Methyl Sodacetylacetate.—L. Bouveault and A. Bongert.

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Journal de Pharmacie et de Chimie,
Series 6, Vol. xii., Nos. 9 and 10.

These two numbers contain no matter of chemical interest.

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Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxiii., No. 22.

Composition of the Orange Pigment of Uraster rubens.—Dr. A. B. Griffiths and F. W. Warren.—The analysis of this pigment has given the following results:—

I. Substance used	0·2460 grm.
CO_2	0·5786 „
H_2O	0·1344 „
II. Substance used	0·0855 „
Volume of nitrogen	13·75 c.c.
Barometric pressure	758 m.m.
Temperature	19° C.

	Found. I.	Found. II.	Calculated for $C_{16}H_{18}N_4O_2$.
Carbon	64·15	—	64·43
Hydrogen	6·07	—	6·04
Nitrogen	—	18·5	18·90
Oxygen	—	—	10·63

These results answer to the formula $C_{16}H_{18}N_4O_2$. Solutions of this pigment (urasterine) do not give any characteristic absorption bands in the spectroscope.

No. 23.

Combustible Gases in the Air. The Presence of Free Hydrogen in the Atmosphere.—Armand Gautier.—Already noticed.

MISCELLANEOUS.

Royal Institution.—On Thursday next, April 16th, Dr. Allen Macfadyen will deliver the first of a course of six lectures at the Royal Institution on "Cellular Physiology," with special reference to the Enzymes and Ferments. On Thursday, April 18th, Mr. Roger Fry will begin a course of two lectures on "Naturalism in Italian Painting," and on Saturday, April 20th, Mr. John Young Buchanan will deliver the first of a course of three lectures on "Climate—its Causes and its Effects." The Friday Evening Discourse on April 19th will be delivered by Professor J. J. Thomson, his subject being "The Existence of Bodies Smaller than Atoms."

New Compounds of Bromide of Aluminium with Organic Substances.—M. Konovalof and V. Plotnikof.—The authors have already described the compounds

$AlBr_3.CS_2C_2H_4Br_2$ and $CS_2(C_2H_5Br.AlBr_3)_2$. The second of these substances, not being crystallisable, is rather unstable, and the results of the analysis do not agree very well with the formula. The ebullioscopic method in bromide of ethyl has given:—Solution at 6 per cent, M=940 (instead of 828); solution at 20 per cent, M=1778; thus in concentrated solutions the molecules are doubled. If to 1 molecule $AlBr_3$, dissolved in an excess of CS_2, we add 1 molecule of bromoform, an oily layer is gradually formed; at 20° it goes on increasing for several months; at about 40° to 45° the reaction is more rapid, and the oily mass becomes crystalline. To obtain the crystals in a pure state it is necessary to leave the mass at 30° for several months in sealed tubes, then wash with bromide of ethyl, and dry in a current of CO_2. The crystals have the appearance of platinocyanide of barium, and are polychromatic. Their fusing-point is 120·7—121·3°; they are insoluble in benzene, CS_2, bromoform, and bromide of ethylene; slightly soluble in bromide of ethyl, and fairly soluble in dry ether; their composition is $CS_2AlBr_3CHBr_3$. Water decomposes this body according to the equation—

$$CS_2-AlBr_3-CHBr_3+4H_2O=$$
$$=Al(OH)_3+5HBr+CO<\begin{matrix}S\\S\end{matrix}>CHBr.$$

The product $COS_2.CHBr$ forms colourless crystals fusible at 52—52·5° with decomposition. With bromide of ethylidene and tribromopropane we obtained in the same manner the compounds $CS_2AlBr_3C_2H_4Br_2$ and $CS_2AlBr_3C_3H_5Br_3$, the latter not crystallised.—*Journ. Soc. Chim. Phys. R.*, vol. xxxi., p. 1020.

The Critical Temperature of some Sulphurised Organic Compounds.—L. Ferretto.—Altschul's method was used for the following bodies:—C_2H_5SH; $CH_3>CH-CH_2-CH_2SH$; $(CH_3)_2S$; $(C_2H_5)_2S$; $(C_2H_5.CH_3)S$. The compounds $(C_2H_5)_2S_2$, $(C_5H_{11})_2S$, and $(C_3H_5)_2S$ were decomposed at a high temperature, and the critical point was determined by the method of mixtures, using Pawlewski's formula. The following results were obtained:—Ethylic mercaptan, 228°; sulphide of methyl, 231·2°; sulphide of ethyl, 284·67°; sulphide of ethyl and methyl, 259·66°; sulphide of isoamyl, 391°; sulphide of allyl, 380°; and isoamylic mercaptan, 334° (?). Pawlewski's law relative to the constant difference between the critical temperature and the boiling-point was confirmed very exactly by the first four, $(\theta-t)=191·8°$ to 193·9°, and not quite so well with the last four, $(\theta'-t)=176°$ to 241°. Guldberg's law (the constant relation $C=\frac{273+\theta}{273+t}$) was closely verified, C=1·38 to 1·63. By comparing these compounds with their analogues in which the S is replaced by O, we find for the sulphydrates that the critical temperature is lower by 14·3° to 16°; with the sulphides, on the other hand, it is higher by 92° to 101·6° and with bisulphide of ethyl we obtain +181·76=2×90·88°; that is to say, about double that observed in the case of the sulphides.—*Gazz. Chim. Ital.*, vol. xxx., p. 296.

Compounds of Uranic Acid with Sulphurous Acid.—V. Kohlschutter.—The author regards these compounds not as salts of the sub-oxide of uranium, UO_2 (with U=240), but as mixed or complex acids. The most simple of these compounds was described by Girard in 1852; it is the body $UO_3SO_2.4H_2O$, soluble in an excess of sulphurous acid, from which it separates in felted green needles, insoluble in pure water. It loses 14·85 per cent of water at 105°, that is 3·5 H_2O. Its formula may therefore be written $O(UO_2.SO_3H)_2+7H_2O$. Its solution either in an excess of sulphurous acid, water, or alcohol no doubt contains $SO_3(UO_2.SO_3H)_2$, that is to say, $2UO_3.3SO_2.H_2O$. The alcoholic solution, treated with ether, gives a yellowish-green flocculent precipitate, which, when drained, dries very rapidly, and then suddenly deliquesces, giving off SO_2. On the addition of SO_3KH to the solution of sulphite of uranium in SO_2, heated on the water-bath, a more or less crystalline anhydrous precipitate is obtained, which may be expressed as $2UO_3.3SO_2.K_2O$ or $SO<\begin{matrix}O-UO_2-SO_3K\\O-UO_2-SO_3K\end{matrix}$. In the same manner the salts of $(NH_4)_2O$ and Na_2O may be obtained. By operating in the same way Scheller obtained salts to which he assigned the general formula $UO_2(OH)SO_3M$; however, the author has never been able to obtain these salts. If we heat the salt $UO_3.SO_2.4H_2O$ on the water-bath, with a quantity of SO_2, insufficient to dissolve it entirely, the green solution becomes yellow, as also does the crystalline deposit of long, pointed, microscopic prisms, whose composition is $UO_3.SO_2.2·75H_2O$ or $(UO_3)_4(SO_2)_4+11H_2O$; the anhydrous compound may be expressed thus:—$SO_3<\begin{matrix}UO_2.SO_3.UO_2\\UO_2.SO_3.UO_2\end{matrix}>SO_3$. By operating in the same manner with the amorphous precipitate obtained from SO_3KH with a solution of sub-nitrate of uranium, we obtain a green micro-crystalline precipitate in rhomboidal tables, consisting of $4UO_3.5SO_2.K_2O$ after desiccation at 105°; the same salts have been obtained with NH_4 and Na, and they may be expressed $SO_3<\begin{matrix}UO_2-SO_2-UO_2-SO_3M\\UO_2-SO_3-UO_2-SO_3M\end{matrix}$. These salts are decomposed by water, giving a green solution and a pulverulent yellow deposit. The green solution gradually deposits the salt $UO_3SO_2.4H_2O$, and the composition of the pulverulent deposit is $3UO_3.2SO_2.K_2O$, or $UO_2<\begin{matrix}UO_3-SO_3K\\UO_3-SO_3K\end{matrix}$. This same salt is deposited from the acid mother-liquor of $4UO_3.5SO_2.K_2O$ when all the excess of SO_2 is evaporated off. We can also obtain the salt $3UO_3.2SO_2.K_2O$ by gradually adding a solution of SO_3K_2 to a solution of sub-nitrate of uranium. When we treat uranic hydrate or one of the above compounds with an excess of an alkaline bisulphite, we obtain a salt with the composition $UO_3.2SO_2.M_2O$, or $UO_2<\begin{matrix}SO_3M\\SO_3M\end{matrix}$. The salt of NH_4 is a green crystalline precipitate composed of microscopic tables. The salt of potassium is formed of bisected prisms.—*Lieb. Ann. Chem.*, vol. cccxi., p. 1.

MEETINGS FOR THE WEEK.

Tuesday, 16th.—Royal Institution, 3. "On Cellular Physiology, with special reference to Enzymes and Ferments," by Allan Macfadyen, M.D., B.Sc.
—— Society of Arts, 4.30. "The True Principles of Stage Scenery," by Percy Fitzgerald, M.A., &c.
Wednesday, 17th.—Society of Arts, 8. "The Synthesis of Indigo," by Prof Raphael Meldola, F.R.S.
—— Microscopical, 8. A Demonstration on the Metamorphoses of *Æschnacyanea*, illustrated by Photographs from Life, by Fredk. Enock, F.L.S., F.E.S.
Thursday, 18th.—Royal Institution, 3. "Naturalism in Italian Painting." by Roger Fry.
—— Society of Arts, 4.30. "Madras, the Southern Satrapy," by John David Rees, C.I.E.
—— Chemical, 8. "Researches on Moorland Waters—Part II., On the Origin of the Combined Chlorine," by W. Ackroyd. "Robinin, Violaquercitrin, and Osyritrin," by A. G. Perkin. "Preparation of Orthodimethoxybenzoin, and a New Method of Preparing Salicylaldehydemethylether," by J. C. Irvine. "Action of Alkyl Haloids on Aldoximes and Ketoximes" (Part II.), and "The Supposed Existence of Two Isomeric Triethyloxamines," by Wyndham R. Dunstan and E. Goulding. "Nitrocamphene, Aminocamphene, and Hydroxycamphene" and "Action of Hydroxylamine on the Anhydrides of Bromonitrocamphane," by M. O. Forster. "The Influence of Cane-sugar on the Conductivities of Potassium Chloride and Potassium Hydroxide, with evidence of Salt Formation in the latter case," by C. J. Martin and O. Masson.
Friday, 19th.—Royal Institution, 9. "The Existence of Bodies Smaller than Atoms," by J. J. Thomson, M.A., &c.
Saturday, 20th.—Royal Institution, 3. "Climate, its Cause and Effects," by John Young Buchanan, M.A., F.R.S.

THE CHEMICAL NEWS.

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HINTS ON TESTING TOOL-STEEL.

By SERGIUS KERN, M.E., St. Petersburg.

It is rather strange that having most elaborate rules and specifications for testing steel used for structural and mechanical purposes, we have no rules for testing tool-steel, except well-known empirical tests, which are less useful to those who are engineers than to well experienced workmen. The results obtained are quite dependent on the individuality of the workman.

Engineers daily test different specimens of soft and medium steel, and having the results of tensile strength and elongation, may judge with great certainty upon the suitableness of the material.

Tool-steel, taking into consideration the percentage of carbon, could be also tested for a certain tensile strength and elongation. Such tests should not exclude the forging and hardening tests, but, made together at one time, are able to give a basis for further development of rules for testing tool-steel delivered by different firms to Government establishments, which usually test the products they buy. But for tool-steel the rules are thoroughly empirical, and cause at present much confusion to the establishments and to the producers.

This is a very serious question, especially if we think that, more often than is believed, we receive, instead of crucible tool-steel, hard open-hearth steel. Some of the latter tool-steel, delivered for certain purposes as good tool-steel, was found by us to be not only too soft, but, being used as a turning tool for cast-iron and bronze, freely crumbled on its sharp edge. The steel analysed contained 0·90 per cent of carbon, 0·39 per cent of manganese, and 0·07 per cent of silicon, and thus showed its origin. Good tool-steel never contains so much manganese, and the small percentage of silicon confirmed the view that the steel was melted by open-hearth process and not in crucibles. Crucible steel has been my speciality for about twenty-five years, and I never saw crucible tool-steel with less than 0·14 per cent of silicon. It is well known that a nearly definite percentage of silicon and carbon is taken by the melting charge from the crucible. Some inferior tool-steels made in crucibles contain the above-mentioned percentage of manganese, but it is a mistake to produce such steels by the dear crucible process. Good tool-steel contains, as maximum, 0·25 per cent of manganese.

The following shows some results of my experiments on crucible and open-hearth tool-steels:—

Crucible.

Percentage of carbon.	Tensile strength in tons per sq. in.	Elongation in 2 ins.	Contraction of area.
		Per cent.	Per cent.
0·60	45	12	30
0·80	58	6	14
0·90	62	5	12

Open Hearth.

0·60	42	15	50
0·80	50	12	28
0·90	55	10	23

Besides carbon the steels contained:—

Crucible—Manganese, 0·25 per cent; silicon, 0·16 per cent; sulphur + phosphorus, 0·03 per cent.

Open Hearth—Manganese, 0·42 per cent; silicon, 0·08 per cent; sulphur, 0·01 per cent; phosphorus, 0·04 per cent.

These experiments may be taken only as a commencement of the question of testing tool-steel mechanically, but speaking generally, hard open hearth tool-steel has the following well-defined properties:—It has less tensile strength as compared with crucible steel of the same percentage of carbon, has a well marked tendency to temper badly after being hardened, and tools made of such steel, under impact, very soon crumble on their sharp edge: the latter defect I entirely attribute to high percentages of manganese (0·35—0·45), which always are found in open hearth tool-steel, and are essential to the process itself. The more oxidised open hearth steel demands more manganese.

ON A TITANIFEROUS IRON ORE FROM NORWAY.

By NICHOLAS J. BLUMAN.

I have recently analysed a titaniferous iron ore from Norway, with the following result:—

Ferrous oxide	40·01 = 31·1 % Fe.	
Titanic acid	43·75	
Magnesia	3·11	
Manganous oxide	0·23	
Alumina	4·00	Gangue.
Silica	8·90	Gangue.
	100·00	

The ore contained crystals aggregated in rosette-like groups; fracture conchoidal, hardness 6, specific gravity 5·163, streak black, and slightly magnetic.

THE ACTION OF IODIC ACID ON URIC ACID, AND THE ESTIMATION OF URIC ACID.

By H. BOUILLET.

If we cause an excess of iodic acid to act on uric acid in the presence of water, we observe, when the temperature is raised, that gas is given off and iodine set at liberty. The reaction is complete at boiling-point. If we collect and weigh the gas and the iodine, we find that the gas is carbonic acid, and that five molecules of uric acid give off five molecules of carbonic acid, while a double atom of iodine is set free.

If, instead of using an excess of iodic acid, we take the theoretical quantity, the reaction is incomplete. The uric acid is not entirely decomposed, and the liquid, which was acid, colourless, and limpid in the first operation, is neutral and rose-coloured in the latter case. This rose-coloured liquid, when evaporated to dryness, leaves a residue which, when taken up with boiling alcohol at 90°, gives alloxane, which can be precipitated with ether.

The alloxane has been recognised by the reactions described by Krasser. The red aqueous solution eventually becomes colourless; it stains paper and albumenoid matters, first yellow, then purple, passing to violet on the addition of ammonia. If, to the clear colourless liquid resulting from the action of the excess of iodic acid on the uric acid, we add baryta-water, an abundant precipitate is formed and ammonia is given off. This precipitate, treated with dilute acetic acid, is partially dissolved and insoluble iodate of barium remains; this is filtered off, and the filtrate neutralised with ammonia. After standing for a few hours, the liquid gives crystals, of which the analysis answers to the formula of mesoximidate of barium,—

$$\begin{matrix}(CO)_3{-}N\\(CO)_3{-}N\end{matrix}\!\!>\!Ba\,3H_2O.$$

	Theory.	Found.
Water of crystallisation ..	13·95	14·00
Carbon	18·60	18·66
Nitrogen	7·235	7·26
Barium	35·4	35·32

With this body we can obtain the mesoximide by precipitating the barium with the theoretical quantity of sulphuric acid. On evaporation, a viscous amber-coloured substance is obtained, crystallising in anhydrous acetone, decomposing slowly in the dark, rapidly in the light, and very hygroscopic; when neutralised with baryta-water, the original salt is formed. Its aqueous solution is acid, it reduces nitrate of silver, and forms a mirror when heated. When boiled for some time with HCl, carbonic acid is given off and oxalic acid formed.

To the liquid containing the products of decomposition of uric acid and free iodic acid, baryta-water is added as before, the precipitate of iodate and mesoximidate of barium is removed, a current of carbonic acid is passed through the liquid, which is heated rapidly to boiling; to this liquid freed from baryta, soda and hypobromite of soda are added, when nitrogen is given off in the cold. The solution, treated with soda and brought to boiling-point, gives off ammonia, which is characteristic of urea. From a consideration of all these reactions and estimations, we have deduced the following course of the reaction:—

Iodic acid decomposes uric acid, giving first alloxane and urea, $C_5H_4N_4O_3+O+H_2O=C_4O_4N_2H_2+CON_2H_4$; then the alloxane itself is hydrated, carbonic acid is given off, and the ammonia combines with the excess of iodic acid, and nothing remains but the mesoxalic group in the state of amide, $C_4O_4N_2H_2+H_2O=CO_2+NH_3+C_3O_3NH$. The final equation shows the action of the iodic acid on uric acid, viz.,—

$$5C_5H_4N_2O_3+I_2O_5+10H_2O=$$

$$=5\left\{\begin{matrix}CO\\|\\CO\\|\\CO\end{matrix}\right\}NH+5CON_2H_4+5CO_2+5NH_3+I_2.$$

This equation agrees with all the experiments and results obtained.

Estimation of Uric Acid.

According to the preceding equation, we observe that, to estimate uric acid by means of this reaction, we can either determine the iodine, as in Causse's method, or the carbonic acid, or again the amount of iodic acid decomposed by the uric acid; the last is the method we adopted. As will be seen, it obviates the separation of the iodine, which is necessary when using Causse's method.

Causse's Method.—The uric acid is precipitated in the form of insoluble urate of barium, the washed precipitate is introduced into a retort with a solution of iodic acid, the retort is connected with a condenser and a flask containing iodide of potassium. On distilling, the iodine is volatilised, and then dissolves in the iodide; the iodine is estimated by means of a N/100 solution of hyposulphite of soda, of which 1 c.c. = 0·00419 of uric acid.

Bouillet's Method.—This method requires a titrated solution of iodic acid and N/10 hyposulphite of soda. To make the iodic acid solution, weigh out 1 grm. of iodic acid, dissolve it in 100 c.c. of distilled water, measure out 10 c.c. of this solution, and add to it 10 c.c. of 1/10th HCl, 30 c.c. of 1/10th KI, and 200 c.c. of distilled water; titrate the iodine set free with a N/10 solution of hyposulphite, and note the volume, V, of hyposulphite used.

Estimation of Uric Acid.—Precipitate the uric acid in the form of insoluble urate of barium by adding to 100 c.c. of urine, previously neutralised with soda, chloride of barium until no more precipitate is formed, then acidulate with 5 c.c. of acetic acid at 1/100th, let stand for fifteen or twenty minutes, filter, and wash the precipitate, which consists of urate, phosphate, and sulphate of barium; wash the precipitate into a porcelain crucible, using about 100 to 150 c.c. of water; add 20 c.c. of H_2SO_4 at 1/10th, so as to set free the uric acid, then boil. At this moment add 10 c.c. of the titrated solution of I_2O_5, and keep boiling gently until the whole of the iodine is liberated. Sometimes the liquid remains yellow, on account of the presence of the last traces of iodine, which are difficult to remove; this, however, can be easily effected by adding a little marble—the carbonic acid given off carries the iodine with it. After cooling, titrate the undecomposed I_2O_5; for this purpose, 10 c.c. of HCl at 1/10th and 30 c.c. of KI at 1/10th are successively added to the cold solution, and the iodine set at liberty is titrated with N/10 hyposulphite. The difference between the original volume of the hyposulphite solution, V, and the present volume, v, gives the amount of iodic acid decomposed; this difference multiplied by the factor 0·007 gives the weight of uric acid. In a general way, the formula is $(V-v)\times 0{\cdot}007=$ uric acid.

The process we have just described has the advantage over the methods of precipitation of the uric acid by salts of silver and copper of not including the xanthic compounds in the estimation. Further, in estimating the amount of iodic acid decomposed, the operation is both simple and rapid, and as for its accuracy, the following table shows that the figures obtained are very close to those given by the Causse method, and nearer the truth than those given by the Salkowski method, which we used as a check.

Urine.	Salkowski.	Causse.	Bouillet.
100 c.c.	0·0285	0·0304	0·0305
100 ,,	0·0510	0·0525	0·0524
100 ,,	0·0415	0·0429	0·0430

Weight of uric acid used.	Causse.	Bouillet.
0·04	0·0394	0·0392
0·04	0·0402	0·0406
0·06	0·0603	0·0595
0·06	0·0595	0·0609

Urine. No.	Uric acid, total weight.	Weight of uric acid found, exceeding 0·0258.	Weight of uric acid added.
0.	0·0258	0	0
1.	0·0355	0·0097	0·01
2.	0·0410	0·0152	0·015
3.	0·0457	0·0199	0·02
4.	0·0511	0·0253	0·025
5.	0·0760	0·0502	0·05

—*Bull. Soc. Chim.*, Series 3, vol. xxv, No. 5.

SILICIDES OF IRON.

By AD. JOUVE.

The presence of silicon in metallurgical products has always been known, and for some time past attempts have been made commercially to obtain alloys containing a large proportion of silicon, both from blast-furnaces, when the proportion hardly exceeds 10 or 12 per cent of silicon, or by means of the electric furnace, when as high a figure as 50 per cent is reached.

In what state does the silicon exist in these ferro silicons?

This question has already been closely studied. MM. H. Sainte-Claire Deville and Caron have obtained silicised castings, but of no definite composition. Winkler, by direct combination, obtained silicised iron which was non crystalline. Carnot and Goutal, in 1897, during a research on the conditions in which the elements existed in metallurgical products, observed the presence of FeSi, and suspected the existence of other products, such as Si_2Fe_3 and Si_2Fe_5, without, however, having isolated these compounds.

By direct combination, M. Moissan obtained the body Fe_2Si perfectly definitely.

The silicide FeSi obtained by Fremy and Hahn, then by Carnot and Goutal, was prepared in the crystalline state by M. Lebeau by means of the reciprocal action of silicides of copper and of iron.

Other silicides have also been described, such as $FeSi_2$ and Fe_3Si_2, which, according to M. Chalmot, are the only ones which exist in commercial ferro-silicons.

The Silicide Fe_2Si.—The existence of this compound has been perfectly well shown by the recent work of M. Lebeau on ferro-silicons containing about 20 per cent of silicon.

All the experiments I had previously made confirm the results obtained with Fe_2Si, the existence of which is beyond question. With some samples we are able to obtain it directly in well-crystallised prisms.

The Silicide FeSi.—This silicide is the one found whenever the proportion of silicon exceeds 25 per cent.

Ferro-silicons containing a higher proportion than 25 per cent give tetrahedric crystal (33·3 per cent silicon), sometimes macled, forming a long series, the whole consisting of a mass of variable richness.

This silicide is also found perfectly crystallised in regular tetrahedra, and the following figures show the composition of some I obtained at the factory at Bozel (Savoy) of the Compagnie-Générale d'Electro-Chimie.

		Theory.
Fe	68·37	66·67
Si	30·08	33·33
C	1·41	—

These crystals sometimes contain a little calcium, sulphur, and phosphorus. The following is a typical complete analysis:—

Iron	67·17
Silicon	29·41
Carbon	1·230
Sulphur	0·012
Phosphorus	0·116
Calcium	1·840

In these commercial ferro-silicons we frequently find 0·7 to 3·0 per cent of carbon.

The compound FeSi can be obtained in a state of purity by taking a rich ferro-silicon and melting it with silica which combines with the carbon. The crystals which are separated give the following figures:—

Si	33·10	33·21
Fe	66·86	66·74

The Silicide $FeSi_2$.—The existence of this compound, obtained by M. Chalmot, is somewhat doubtful. I have never been able to isolate it directly from any commercial ferro-silicon.

I have used a silicide obtained by the direct union of silicon and iron in the proportion of about 55 per cent Si. This silicide, on slow cooling, allowed the compound FeSi (33·3 per cent Si) to separate out, a much richer ferro-silicon forming the rest of the mass.

On the other hand, an alloy of 41 per cent Si was treated according to M. Chalmot's method by hydrofluoric acid; a residue was obtained with a crystalline appearance which answered roughly to the formula $FeSi_2$. Four analyses gave:—Si = 54·28, 48·76, 51·01, and 44·94; theory for $FeSi_2$ requires 50·0 per cent Si.

Under the microscope, these crystals were very slightly characteristic, irregular, and non-homogeneous.

The same products, treated with a hot concentrated solution of soda, lost silicon and left a powder of a crystalline appearance, containing Si = 30·47, 31·28, 30·98, and 32·16; theory for $FeSi_2$ requires 33·33 per cent Si.

It therefore appears as if this product, $FeSi_2$, is nothing more than a simple alloy or mixture of FeSi and Si.

The result of what has been stated above seems to show that commercial ferro-silicons contain the silicon in the form of mixtures of the two definite compounds Fe_2Si and FeSi, with variable proportions of iron or of silicon.

The compounds Fe_3Si_2 and Fe_5Si_2 have not been obtained in a distinct crystalline form; their existence is very doubtful and quite hypothetical.

In conclusion, I would remark that the alloys used by me were obtained by the direct reduction of silica by carbon, as was also the silicon used for the direct formation of the products containing proportions near to 50 per cent.

The factory at Bozel (Savoy), where these products were made, has since our research made a speciality of the manufacture of ferro-silicons, no longer as laboratory experiments, but at the rate of several tons a day of products rich in silicon.

Remarks on the presence of Carbon in Ferro-silicons.—It has been shown that crystallised ferro-silicons similar to FeSi contain carbon. The following are a few analyses:—

Fe ..	69·68	69·09	69·33	67·48	67·89
Si ..	28·02	29·11	28·61	31·82	31·11
	(28·02)	(29·05)	(28·63)	(31·77)	(31·05)
C ..	2·28	1·84	2·02	0·67	0·98

We know that 12 of carbon corresponds to 28 of silicon. If we transform the carbon into silicon in this proportion, and subtract this value in silicon of the carbon from the theoretical figure, 33·33 per cent, we obtain the figures given in brackets, which are remarkably close to those found.

The carbon thus appears to enter into the constitution of the crystals, substituting itself for the silicon. It, however, still remains to be determined in what state it really exists.—*Bull. Soc. Chim.*, Series 3, vol. xxv., No. 6.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MARCH 30TH, 1901.

By SIR WILLIAM CROOKES, F.R.S., and PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E., *Water Examiner, Metropolis Water Act*, 1871.

London, April 10th, 1901.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 208 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from March 1st to March 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 208 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during the month has been 1·44 inches; the average fall for the last thirty-five years is 1·47 inches; this leaves a deficit of 0·03 inch, making the total deficit for the year 1·56 inches, or 29·1 per cent on the thirty-five years' average.

Our bacteriological examinations of 545 samples have given the results recorded in the following table; we

have also examined 38 other samples, from special standpipes, &c., making a total of 583 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	593
New River, filtered (mean of 131 samples) ..	10
Thames, unfiltered (mean of 26 samples) ..	2303
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 295 samples)	27
Ditto ditto .. .. highest	448
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 26 samples) ..	315
River Lea, from the East London Company's clear-water wells (mean of 41 samples) ..	43

Of the 467 samples of impounded and filtered water supplied to London, examined bacteriologically during the past month, twenty samples, or 4·2 per cent, were sterile. Only ten samples out of the total number examined contained more than 150 microbes, and twenty-nine samples, or 6·2 per cent, contained more than 100 microbes per c.c. The mean of the microbes in the excess samples was 162, as against a corresponding mean last month of 151.

Nearly the whole of the excess results occurred during the early part of the month, when the climatic conditions were unusually exceptional.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

SOME PRINCIPLES AND METHODS OF ROCK ANALYSIS.*

By W. F. HILLEBRAND.

(Continued from p. 178).

XII. *Titanium* (continued).

Gooch's Gravimetric Method.

When titanium is present in excess of 4 to 5 per cent, and whenever for any reason it is desired to employ a gravimetric method, among the few that have been thoroughly tested that of Dr. Gooch (*Proc. Am. Acad. Arts Sci.*, New Series, vol. xii., p. 435; *Bull. U. S. Geol. Survey*, 1886, No. 27, p. 16; Chemical News, 1885, vol. lii., pp. 55 and 68), is unequalled. With one or two minor modifications introduced by Dr. T. M. Chatard (*Am. Chem. Journ.*, 1891, vol. xiii., p. 106; *Bull. U. S. Geol. Survey*, No. 78, p. 87; Chemical News, 1891, vol. lxiii., p. 267), it is as follows:—

Any solution of the rock freed from silica can be used, and the first step is to remove the iron. This is best done, after adding tartaric acid, and reducing the iron by means of hydrogen sulphide to the ferrous condition, by rendering the solution ammoniacal, and introducing more hydrogen sulphide. If the iron is not thus reduced before precipitation, titanium will be in part thrown down also (Cathrein, *Zeit. für Kryst.*, 1882, vol. vi., p. 243; 1883, vol. vii., p. 250). The amount of tartaric acid is to be gauged according to the combined weights of the oxides to be held by it in solution, and three times this weight is ample. After removing the iron sulphide by filtration—little washing suffices, because of the relatively small amount of titanium commonly present—the tartaric acid is destroyed as follows:—

Potassium permanganate to the extent of two and one-half times the weight of the tartaric acid used is made into a strong solution, and to the ammoniacal filtrate from the iron sulphide enough sulphuric acid is introduced to leave some excess after all the permanganate has been reduced. After expulsion of hydrogen sulphide by boiling, the permanganate is added gradually to the hot solution contained in a large beaker or flask. A vigorous reaction ensues. When a permanent brown precipitate of manganic hydrate appears the tartaric acid has been fully broken up, and the precipitated manganese is to be re-dissolved by a few drops of ammonium bisulphite or of sulphurous acid solution.

Ammonia is then added in slight excess, followed at once by acetic acid in considerable excess, and the boiling is continued for a few minutes. Thereby the titanium is freed from most of the alumina, and from lime and magnesia if they had not been earlier removed, also from most of the manganese introduced. The precipitate is filtered and washed with water containing acetic and sulphurous acids, then ignited, fused thoroughly with sodium carbonate, and leached with water to remove phosphoric acid and most of the remaining alumina. The residue is again ignited and fused with sodium carbonate. To the cooled melt in the crucible strong sulphuric acid is to be added, wherein it dissolves readily by aid of gentle heat. This solution is to be poured into a small volume of cold water, and the platinum it contains precipitated by hydrogen sulphide at or near boiling temperature. After filtering and cooling, ammonia is added till the titanium is just precipitated, and a measured volume, containing a known weight of absolute sulphuric acid, is then added—just enough to re-dissolve the precipitate. The solution is then made up with acetic acid in such amount that the final bulk shall contain from 7 to 11 per cent of absolute acid, and then enough solid sodium acetate is stirred in to more than take up the sulphuric acid introduced. Upon rapidly bringing the liquid to ebullition the titanium is precipitated in flocculent and easily filterable condition, and the precipitation is complete after a minute's boiling, provided all the prescribed conditions have been followed and zirconium is absent.

The precipitate is washed first with acetic acid of 7 per cent strength, and then with hot water. After fifteen to twenty minutes' ignition over a good burner it is in condition for weighing, and will lose no more weight over the blast-lamp. For large amounts of titanium a repetition of the sodium carbonate fusion, &c., should be made. The actual carrying out of all these operations, when once the method is understood, requires much less time than the detailed description would indicate.

Gooch's Method not Directly Applicable to Rocks containing Zirconium.

Prior to the adoption of the colorimetric method, Dr. Gooch's was invariably used in this laboratory. Occasional inability to secure clean and complete precipitation by it was experienced, especially with a certain series of rocks rather poor in titanium. Long research showed the difficulty to be due to the presence of zirconium, which acts as a marked preventive of the precipitation of titanium by boiling in an acetic acid solution under the conditions of the Gooch method.

The above rocks were found to contain up to 0·2 per cent of ZrO_2, and this amount was able to prevent precipitation of 0·3 per cent of TiO_2. The titanium which came down in excess of this amount did not settle out in flocculent condition, as happens when zirconium is not present, and it was difficult to filter. After the removal of the zirconium in the manner hereafter described (p. 185), however, no difficulty was experienced in precipitating all the titanium with the usual ease.

Superiority of the Colorimetric and Gooch Methods over the Older ones.

In view of the good results obtainable by the colorimeter method in all cases and by the Gooch method in the absence of zirconium, it is incomprehensible that the old method of precipitation by many hours' boiling in a nearly neutral sulphate solution in presence of sulphurous acid should still find adherents in any part of the world.

Attention has been directed (p. 165) to the error resulting

* *Bulletin of the United States Geological Survey*, No. 176.

from attempting to separate aluminum from titanium by either fused or dissolved sodium hydroxide.

Baskerville's Method.

Baskerville (*Journ. Am. Chem. Soc.*, 1894, vol. xvi., p. 427) has proposed the separation of titanium from iron and aluminum by boiling the neutralised solution of the chlorides for a few minutes in presence of sulphurous acid. The test separations as given by him are sharp, and a single precipitation is said to suffice, the titanium being free from iron and easily filterable. This last statement and the ready precipitability are fully confirmed by the experiments of the writer on titaniferous iron ores, but, although the titanium is completely thrown out, it carries with it a little iron, for instance, about 0·25 per cent Fe_2O_3 with 8 to 10 per cent TiO_2. Zirconium would probably be likewise precipitated (see p. 186), and phosphorus perhaps also, but this last point has not been investigated, neither has the applicability of the method to aluminous rocks been tested.

XIII. *Barium (Zirconium, Total Sulphur).*

Reasons for Estimating Barium in a Separate Portion of Rock Powder.—It has been said above (p. 166) that only in very exceptional cases will barium be found with the calcium and strontium after two, or possibly three, precipitations of the latter as oxalate, since it passes into the filtrates with the magnesium, whence it may be obtained as sulphate after removal of ammoniacal salts. Addition of some alcohol insures also the recovery of traces of strontium if the rocks are very rich in it. But it is unsafe to regard the amount thus separated from the magnesium as representing the total amount of barium in the rock. It will almost always be found lower than the truth, probably for the reason that there are opportunities during the analysis for slight losses. It is best to estimate it in a separate 2 grm. portion, which may also serve with advantage for the estimation of zirconium and total sulphur.

Modes of Attack and Subsequent Treatment.—If zirconium and sulphur are not to be looked for, the simplest procedure is to decompose the powder by sulphuric and hydrofluoric acids (see p. 178, under "Titanium"), and to complete the purification of the barium sulphate thus obtained in the manner described in the third paragraph below.

If zirconium and sulphur are both to be likewise determined, decomposition is effected by fusing over the Bunsen flame, and then over the blast with sulphur-free sodium carbonate and insufficient nitre to injure the crucible, first fitting the latter snugly into a hole in asbestos board (Lunge) to prevent access of sulphur from the gas flame. In case sulphur is not to be regarded, the nitre and asbestos board are omitted. After thorough disintegration of the melt in water, to which a drop or two of methyl or ethyl alcohol has been added for the purpose of reducing manganese, the solution is filtered, and the residue washed with a very dilute solution of sodium carbonate free from bicarbonate. This is to prevent turbid washings. A yellow colour in the filtrate indicates chromium.

For the further treatment of the filtrate see "Sulphur," and "Chromium—Colorimetric Method" (*prox.*).

The residue is dissolved in quite dilute warm sulphuric acid (stronger acid may be used if barium only is sought), and filtered through the original filter. This, with its contents, is ignited, evaporated with hydrofluoric and sulphuric acid, and taken up with hot dilute sulphuric acid. The filtrate, added to the former one, now contains all the zirconium (see under "Zirconium" for its further treatment). The residue contains all the barium, besides some of the strontium, and perhaps a good deal of calcium. It is fused with sodium carbonate, leached with water, the residue dissolved off the filter by a few drops of hydrochloric acid, from which solution the barium is thrown out by a large excess of sulphuric acid. A single solution of the barium sulphate in concentrated sulphuric acid and re-precipitation by water suffices to remove traces of calcium which might contaminate it if the rock was one rich in calcium, and even strontium is seldom retained by it in quantity sufficient to give concern. Should this be the case, however, which will occur when the SrO and BaO are together in the rock in, roughly speaking, 0·2 and 0·4 per cent, respectively, the only satisfactory way is to convert the sulphates into chlorides, and to apply to the mixture the ammonium chromate method of separation (p. 166).

Barium and strontium sulphates can be brought into a condition for testing spectroscopically by reducing for a very few moments the whole or part of the precipitate on a platinum wire in the luminous tip of a Bunsen burner, and then moistening with hydrochloric acid. This should be known to everyone, but probably is not.

The procedure outlined in the foregoing paragraphs for the estimation of calcium, strontium, and barium in silicate rocks is the one which long experience has shown to be best adapted for securing the most satisfactory results with a minimum expenditure of time. (For details consult W. F. Hillebrand, *Journ. Am. Chem. Soc.*, 1894, vol. xvi., p. 83; CHEMICAL NEWS, 1894, vol. lxix., p. 147). Even where no attempt is made to separate contaminating traces of SrO and BaO one from the other, the error is usually of no great consequence, for an absolute error of 25 per cent, even, in a substance constituting only one or two tenths per cent of a rock is ordinarily of small moment compared with the ability to certify to its presence with approximate correctness.

With such small amounts of barium as are usually found in rocks it is doubtful if Mar's (*Am. Journ. Sci.*, 1892, 3rd Ser., xliii., p. 521), method for the separation of barium from calcium and magnesium by the solvent action of concentrated hydrochloric acid mixed with 10 per cent of ether on the chlorides, could be conveniently applied here, although for larger amounts the method would seem to be accurate and easily executed. Moreover, it would probably not entirely remove contaminating strontium, and hence offers no advantage.

XIV. *Zirconium.*

This element is rarely looked for by chemists, though shown by the microscope to be one of the most constant rock constituents, usually in the form of zircon, in which occurrence its amount can be approximately judged of and a chemical test rendered almost unnecessary; but sometimes it occurs in other minerals, and is then unrecognisable under the microscope. It may rarely be present up to a few tenths of 1 per cent of the rock.

Author's Method.

For its detection and estimation in such cases, or whenever a search for it seems called for, the following procedure, based on a method by G. H. Bailey (*Journ. Chem. Soc.*, 1886, vol. xlix., pp. 149, 481), has been devised which serves, when carried out with care, to detect with certainty the merest trace—0·02 per cent, for instance—in 1 grm.

The preliminary treatment of the rock powder has been fully given under "Barium," where the separation from barium has been described, and also the concentration of the zirconia in a small amount of very dilute sulphuric solution. This should probably not contain much above 1 per cent of sulphuric acid, though the actually permissible limit has not been established. To the solution, which should be in a small flask, is now added hydrogen peroxide to oxidise the titanium, and then a few drops of a soluble orthophosphate solution. The flask is set aside in the cold for twenty-four to forty-eight hours. If the colour bleaches after a time, more hydrogen peroxide should be added. Under these circumstances the zirconium is thrown out as phosphate, and collects as a flocculent precipitate, which at this stage is not always pure. No matter how small or in-

significant, it is collected on a filter, ignited, fused with sodium carbonate, leached with water, the filter again ignited, fused with very little acid potassium sulphate, brought into solution in hot water with a few drops of dilute sulphuric acid, poured into a flask of about 20 c.m.^{3} capacity, a few drops of hydrogen peroxide and of sodium phosphate added, and the flask set aside. Titanium is now almost never present, and the zirconium appears after a time as a white flocculent precipitate, which can be collected and weighed as phosphate. For the small amounts usually met with it is safe to assume that it contains 50 per cent of ZrO_2 (51·8 by theory). If the amount is rather large, it may be fused with sodium carbonate, leached, ignited, fused with acid potassium sulphate, re-precipitated by ammonia, and weighed as ZrO_2. Certainty as to its identity can be had by again bringing it into solution, precipitating by ammonia, dissolving in hydrochloric acid, evaporating to a drop or two, and testing with turmeric paper or by a microchemical reaction. With the very smallest amounts no colour can be obtained by this turmeric-paper test, which, however, responds readily to as little as 1 m.grm. of dioxide, and with proper care for as small an amount as 0·3 m.grm. (Dr. H. N. Stokes). No element other than thorium is ever likely to contaminate the zirconium thus precipitated.

In Bailey's experiments the precipitation was not made by addition of a phosphate, but is said to be due solely to the hydrogen peroxide, the precipitate being a hydrated peroxide, Zr_2O_5, or ZrO_3 (Bailey, Chemical News, 1889, vol. lx., p. 6). My own efforts to secure a precipitate in acid solutions of zirconium sulphate by hydrogen peroxide alone were unsuccessful, perhaps for lack of a sufficiently strong peroxide. The ability to obtain the zirconium free from phosphoric acid would certainly be a great improvement on the method described above.

Were it not for the necessity of working in a weakly acid solution, the separation of zirconium could be made in the same portion in which the titanium is colorimetrically determined.

Other Methods of Separating Zirconium.

Streit and Franz (*Journ. für Prakt. Chemie*, 1869, vol. cviii., p. 65), claim to secure complete separation of titanium from iron and zirconium by boiling the neutralised solutions of the sulphates with a large excess (50 per cent) of acetic acid. The method has been from time to time recommended, but without any data showing its value. The single separation made by Streit and Franz was far from perfect.

Davis (*Am. Chem. Journ.*, 1889, vol. xi., p. 27) separated zirconium sharply from aluminum, but not from iron, by precipitation as an oxyiodate in a boiling neutralised solution of chlorides, but the method is hardly applicable for rock analysis.

Baskerville (*Journ. Am. Chem. Soc.*, 1894, vol. xvi., p. 475; Chemical News, 1894, vol. lxx., p. 57), has proposed a method for the separation of zirconium from iron and aluminum similar to his method for the separation of titanium from those elements (p. 185). It is based on the precipitability of ZrO_2 by boiling the neutralised chloride solution for two minutes in presence of sulphurous acid, and seems to be excellent. As titanium is always present and is presumably quantitatively thrown down also, the two would have to be separated by hydrogen peroxide. No tests as to the availability of the method for separating the small amounts met with in rock analysis have been made.

XV. *Rare Earths other than Zirconia.*

For the few cases in which it may be necessary to look for rare earths other than zirconia, the following procedure is suggested as likely to prove satisfactory:—

The rock powder is thoroughly decomposed by several partial evaporations with hydrofluoric acid, the fluorides of all earth metals except zirconium are collected on a platinum cone, washed with water acidulated by hydrofluoric acid, and the precipitate washed back into the dish or crucible, and evaporated with enough sulphuric acid to expel all fluorine. The filter is burned and added. By careful heating the excess of sulphuric acid is removed and the sulphates are taken up by dilute hydrochloric acid. The rare earths, with perhaps some alumina, are then separated by ammonia, washed, re-dissolved in hydrochloric acid, and evaporated to dryness, then taken up with water and a drop of hydrochloric acid, and only enough ammonium acetate to neutralise the latter added, followed by oxalic acid (not ammonium oxalate, which would fail to precipitate thorium). In this way as little as 0·03 per cent of rare earths have been found when working on not more than 2 grms. of materials.

This method eliminates at once most of the aluminum, all the iron, phosphorus, titanium, and zirconium, and has the further advantage of collecting with the earthy fluorides, as UF_4, any uranous uranium that the rock might have held.

An alternative method would be to fuse with sodium carbonate, leach with water to get rid of phosphorus as far as possible, dissolve the residue in hydrochloric acid, separate silica as usual, precipitate alumina, &c., by ammonia, dissolve the precipitate again in hydrochloric acid, evaporate, and proceed as by the former method, which in most cases would undoubtedly give better results than this one.

XVI. *Phosphorus.*

It is sometimes possible to extract all phosphorus from a rock by simple digestion with nitric acid, but quite as often, if not oftener, this fails; hence the necessity for resorting to one of the longer methods of extraction detailed below.

Procedure when Material is Ample.

When material is ample it is best to use one portion for phosphorus only, and to proceed as follows:—

Fuse with sodium carbonate, separate silica by a single evaporation with nitric acid, treat the ignited silica with hydrofluoric and a drop or two of sulphuric acids, evaporate to expel hydrofluoric acid, bring the small residue into solution by boiling with nitric acid, and add it to the main portion, in which, after addition of considerable ammonium nitrate, precipitate the phosphorus by molybdate solution.

The turbidity often observed on dissolving the precipitated and washed phospho-molybdate in ammonia is due to a compound of phosphorus. If the addition of a small fragment of a crystal of citric or tartaric acid fails to dissolve it, this should always be re-fused with sodium carbonate, extracted with water, and the filtrate otherwise treated as above, in order to secure the phosphorus in it.

According to Gooch and Austin (*Am. Journ. Sci.*, 1899, Fourth Series, vol. vii., p. 187; *Zeit. für Anorg. Chemie*, 1899, vol. xx., p. 121; Chemical News, 1899, vol. lxxix., pp. 233, 244, 255), in order to secure a magnesium-ammonium phosphate of normal composition, the procedure at this point should be as follows:—To the phosphate solution containing not more than 5 to 10 per cent of ammonium chloride, and a slight excess of magnesia mixture, a little ammonia is added, and the precipitate is washed in due time with weak ammonia water. In general, however, as these conditions can seldom be fulfilled, they recommend to decant the supernatant liquid through the filter which is later to receive the precipitate, to dissolve this in as little hydrochloric acid as possible, to re-precipitate by dilute ammonia without further addition of magnesia mixture, and to wash finally with weakly ammoniacal water. Excess of ammonia, of ammonium salts, and of precipitant are all objectionable. In rock analysis the second precipitation will seldom be necessary. For ignition, &c., of the precipitate, see this subject under "Magnesium" (p. 176).

Procedure when Material is Scanty.

The following procedure admits of determining in the same portion, besides phosphorus, barium, iron, vanadium,

chromium, and titanium, the last two either colorimetrically or gravimetrically, and is in large part extracted from a paper by Dr. T. M. Chatard (*Am. Chem. Journ.*, 1891, vol. xiii., p. 106; *Bull. U. S. Geol. Survey*, No. 78, p. 87; Chemical News, 1891, vol. lxiii., p. 267).

Silica is removed by hydrofluoric and sulphuric acids, excess of fluorine expelled, the residue brought into solution as far as possible with sulphuric or hydrochloric acid and hot water, filtered, the residue ignited, fused with sodium carbonate, dissolved in hydrochloric acid, and the solution, after precipitation of barium, added to the main one, which is now precipitated by ammonia to get rid of the magnesium salts usually present, and thus ensure a cleaner subsequent fusion with sodium carbonate.

The precipitated Al_2O_3, P_2O_5, Cr_2O_3, Fe_2O_3, and TiO_2 is dissolved in hot hydrochloric acid, and filtered into a large platinum crucible, the filter burned and added, the solution evaporated to pastiness, a little water added to dissolve the salts, and dry sodium carbonate added in portions, and stirred in thoroughly to prevent lumpiness in the fusion to follow, which is continued for half-an-hour. Addition of sodium nitrate is not necessary.

The fused mass is boiled out with water, and washed with very dilute sodium-carbonate solution. In the residue iron and titanium can be determined by the methods already described. In the filtrate chromium can be determined colorimetrically if present in sufficient amount to give a pronounced colour (see "Chromium—Colorimetric Method," *prox.*). Afterwards, or immediately if the chromium is not to be thus estimated, enough ammonium nitrate is added to react with all the carbonate, and the solution is digested on the bath till most of the ammonium carbonate is gone. Nearly, if not quite all alumina is thus thrown out, carrying with it all phosphorus. The precipitate is washed with dilute ammonium-nitrate solution till the yellow colour wholly disappears, after which it is dissolved in nitric acid, and the phosphorus thrown out by molybdate solution. The filtrate, containing chromium and vanadium, can be treated as detailed in the next following sections.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 21st, 1901.

Professor Thorpe, C.B., F.R.S., President, in the Chair.

Messrs. G. D. Lander, H. W. Kinnersley, and E. F. Linstead were formally admitted Fellows of the Society.

The following certificates were read for the first time:—William Henry Duckworth, 87, New Bank Road, Blackburn; Samuel Philip Eastick, 25, Woodville Road, Ealing; Ernest Allred Lewis, 310, Dudley Road, Birmingham; Alexander McKenzie, Jenner Institute, S.W.; Edgar Neuman, 10, Randolph Crescent, Maida Vale, London; William Oldershaw, Market Place, Nottingham; Samuel Slefrig, 18, Waterloo Road, Shepton Mallet, Som.; James Smith, 14, Mersey Road, Aigburth, Liverpool.

Reply to the Address to the King.

The Secretary read the following reply which His Majesty the King has been graciously pleased to cause to be made to the Address of the President, Council, and Fellows of the Society:—

Marlborough House,
Pall Mall, S.W.
23rd February, 1901.

The Private Secretary is commanded by the King to thank the President, Council, and Fellows of the Chemical Society, for the kind expression of their sympathy with His Majesty, on the occasion of the lamented death of Her late Majesty the Queen, and for the loyal and dutiful sentiments conveyed in their Address to the King.

Day and Hour of Meeting.

The following is the report of the Committee appointed by the Council to examine the cards returned by Fellows in reply to the question as to the suggested change in the Day and Hour of the Ordinary Meetings to Wednesday, at 5.30 p.m.:—

"Nineteen hundred cards were issued to Fellows, and 1000 answers were returned. Of these, 581 were unreservedly in favour of the change, namely, 256 London Fellows, and 325 Country Fellows. 118 Fellows, whilst not voting unreservedly for the change, said they offered no objection to it. 172 Fellows were unreservedly opposed to the change. Of the 129 Fellows remaining, 85 expressed no objection to the change of day, but offered suggestions as to change of hour. 3 suggested meeting at 3, 1 at 4, 1 at 4.30, 12 at 5, 12 at 6, 9 at 6.30, 10 at 7, 5 at 7.30, 15 at 8, and 2 at 8.30. 11 suggested a later hour than 5.30 without particularising it, and 4 alternately 5.30 and 8. 24 Fellows suggested meeting on some other day than Wednesday or Thursday, namely, 2 on Monday at 5.30, 1 on Tuesday at 8, 14 on Friday, 10 of whom preferred 5.30; of the remaining 4, 2 indicated no preference as to hour, 1 suggested 8, and 1 suggested 8.30. 7 Fellows suggested various hours on Saturday afternoon or evening. 16 Fellows preferred Thursday, but suggested some other hour than 8, 11 suggested 5.30. 1 preferred 6, and 3 preferred 7. 1 suggested 8.30. 4 Fellows deprecated the change on the ground that it clashed with the present arrangements of the Society of Public Analysts.

"Analysing the replies of those Fellows who have contributed papers to the Society, 266 of whom have responded, 188 have voted for the change, and 78 against it."

Of the following papers, those marked * were read:—

*40. "*Researches on Morphine.*" Part II. By S. B. Schryver and F. H. Lees.

The authors have shown (*Trans.*, 1900, lxxvii., 1024), that bromomorphide, $C_{17}H_{18}O_2NBr$, is decomposed by water in accordance with the equation—

$$C_{17}H_{18}O_2NBr + H_2O = C_{17}H_{19}O_3N,HBr,$$

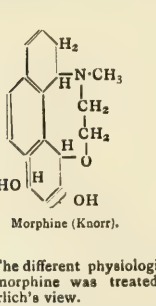
and from the reaction product a new base, isomeric with morphine, and designated *isomorphine*, was isolated and described. The authors have since isolated from the product of the above reaction another new base, *β-isomorphine*, $C_{17}H_{19}O_3N$, which is formed only in relatively small amount. It crystallises from alcohol in double pyramids of the formula $2C_{17}H_{19}O_3N,C_2H_6O$, which, after drying at 120° melt at 182°, and for which $[\alpha]_D$ 17° = −216·2°. Chloromorphide, when decomposed by water, also yields *β-isomorphine*, together with another base which has not yet been further examined. In view of the non-narcotic action of *iso*morphine as compared with morphine, experiments were carried out to determine the chemical relationship between the two isomerides. *iso*Morphine yields a *diacetyl* *isomorphine methiodide*, $C_{17}H_{17}(O{\cdot}CH_3CO)_2ONCH_3I$, as needles melting at 242° with decomposition. Phosphorus tribromide reacts with *iso*morphine, giving bromomorphide (m. p. 170°) identical with that obtained from morphine by the same reaction. Phosphorus trichloride, on the other hand, reacts with *iso*morphine, yielding no definite product, whereas chloromorphide results from the same reaction with morphine. iso*Codeine methiodide*, $C_{17}H_{18}O_2(OCH_3)NCH_3I$, forms leaflets melting at 265° with decomposition, and for it $[\alpha]_D$ 17° = −102·1°. It was prepared by the three following methods: (*a*) by the action of silver sulphate and barium hydroxide on *iso*morphine methoidide, with subsequent interaction of the resulting methydroxide and methyl iodide; (*b*) by the action of excess of methyl iodide on the sodium derivative of *iso*morphine; (*c*) from codeine by the following steps: *bromocodeide*, $C_{17}H_{17}O(OCH_3)N{\cdot}Br$, prepared by the action of phos-

phorus tribromide on codeine, forms pearly scales melting at 162°, for which $[\alpha]_D\ 20° = +56{\cdot}7°$; *isocodeine*, $C_{17}H_{18}O_2(OCH_3)N$, from the action of water on bromocodeide, which forms needles melting at 144°, for which $[\alpha]_D\ 13° = -169°$. The methiodide was then readily prepared from *iso*codeine.

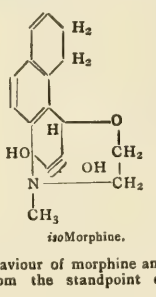
The formation of *iso*codeine methiodide by the above methods confirms the phenolbetaine constitution,—

$$C_{16}H_{15}O_2\overset{O}{\underset{N(CH_3)_2}{<}},$$

for *iso*morphine methydroxide, which was provisionally assigned to this substance by the authors in their previous paper. Sodium hydroxide reacts with *iso*codeine methiodide, yielding the base *methi*-iso*morphimethin*, $C_{16}H_{14}O_2(OCH_3)\cdot N(CH_3)_2$, which forms tables melting at 167°, and having $[\alpha]_D\ 20° = +64{\cdot}6°$. *Methi*-iso*morphimethin methiodide*, $C_{16}H_{14}O_2(OCH_3)\cdot N(CH_3)_3I$, forms needles melting at 265°, and for which $[\alpha]_D\ 17° = +34{\cdot}7°$. *Methi*-iso*morphimethin methydroxide* is split up by the action of heat, and yields morphenol methyl ether, $C_{15}H_{10}O_2$, m. p. 65°, which is identical with the phenol obtained by Knorr (*Ber.*, 1889, xxii., 183), from codeine methiodide, the morphine derivative, by analogous reactions to the above. These results indicate the presence in *iso*morphine of exactly the same groups as occur in morphine, and the authors suggest that the relationship between these two bases is, in all probability, similar to that represented by the two following formulæ:—



Morphine (Knorr).



*iso*Morphine.

The different physiological behaviour of morphine and *iso*morphine was treated of from the standpoint of Ehrlich's view.

"41. "*The Constitution of Pilocarpine.*" Part II. By H. A. D. Jowett, D.Sc.

When bromine acts on *iso*pilocarpine in acetic acid solution, dibromo*iso*pilocarpine perbromide is formed as the chief product of the reaction, but small quantities of monobromo*iso*pilocarpine and *iso*pilocarpinic acid are also produced. *Dibromoisopilocarpine perbromide*, $C_{11}H_{14}O_2N_2Br_2\cdot HBr_3$, crystallises in needles melting at 165°. Treated with ammonia, *dibromoisopilocarpine*, $C_{11}H_{14}O_2N_2Br_2$, is formed, crystallising in rectangular prisms melting at 135°. It is optically inactive, and is only feebly basic, being precipitated from its solution in strong acids by water; it does not react with methyl iodide. On reduction, it is converted into *iso*pilocarpine. *Monobromoisopilocarpine*, $C_{11}H_{15}O_2N_2Br$, forms needles melting at 164°. Iso*pilocarpinic acid*, $C_{11}H_{16}O_4N_2$, was only obtained as an oil. It yields a microcrystalline barium salt $(C_{11}H_{15}O_4N_2)_2Ba$, and is therefore monobasic.

Dibromo*iso*pilocarpine, on oxidation with permanganate, yields hydrobromic acid, ammonia, methylamine, a new acid termed *pilopinic acid*, $C_8H_{11}O_4N$, and the acid, $C_7H_{10}O_4$, previously described, and which is now called pilopic acid.

Pilopinic acid, $C_8H_{11}O_4N$, is crystallised with difficulty, forming pearly plates melting at 98°. It is lævorotatory $[\alpha]_D = -13{\cdot}6°$. It is a monobasic lactonic acid. The monoethyl ester boils at 262° at 10 m.m. On oxidation it yields ammonia and pilopic acid.

When bromine acts on *iso*pilocarpine in aqueous solution at 100° in a sealed tube, the following products are formed: — Dibromo*iso*pilocarpinic, monobromo*iso*pilocarpinic, bromopilopinic, and bromopilopic acids, ammonia and methylamine, the two first-named acids being the chief products formed in about equal quantities.

Dibromoisopilocarpinic acid, $C_{11}H_{14}O_4N_2Br_2$, forms rectangular crystals melting at 235°. The acid is dextrorotatory $[\alpha]_D = +24{\cdot}4°$, and is monobasic.

Monobromoisopilocarpinic acid, $C_{11}H_{15}O_4N_2Br$, has only been obtained as a syrup.

When dibromo*iso*pilocarpinic acid is treated with sodium amalgam in alcoholic solution, pilopic acid is formed. This acid, previously described as an oil, has now been obtained in crystals melting at 103°. Both mono- and dibromo-*iso*pilocarpinic acids, on reduction with zinc and glacial acetic acid, yield a new crystalline lactone, *isopilocarpinolactone*, $C_{11}H_{14}O_4N_2,H_2O$, which forms rectangular prisms which melt at 83°. It is lævorotatory, $[\alpha]_D = -51{\cdot}9°$, and is a neutral substance which reacts with strong alkalis, forming salts of hydroxy*iso*pilocarpinic acid, $C_{11}H_{16}O_5N_2$, which are stable. It does not unite with methyl iodide, even when heated in alcoholic solution at 100°.

Dibromopilocarpine, $C_{11}H_{14}O_2N_2Br_2$, first prepared by Pinner and Kohlhammer (*Ber.*, 1900, xxxiii., 1424), has been further studied; it melts at 95° when pure, and not at 79° as stated by these authors. It is dextrorotatory $[\alpha]_D = +43{\cdot}6°$, and, like its isomeride dibromo*iso*pilocarpine, is very feebly basic, and does not unite with methyl iodide. On reduction, it is converted quantitatively into pilocarpine.

Efforts to prepare bromocarpinic acid, first described by the above authors, have been unsuccessful, and results have been obtained which indicate that the first action of bromine on pilocarpine at 100° under pressure is analogous to that on *iso*pilocarpine. The bromopilocarpinic acids on reduction, however, yield pilocarpinic acid, $C_{11}H_{16}O_4N_2$, thus differing from the bromo*iso*pilocarpinic acids.

Experiments on the oxidation and attempted reduction of *iso*pilocarpine were also described.

"42. "*The Chemical Action of Bacillus Coli Communis and Similar Organisms on Carbohydrates and Allied Compounds.*" By A. Harden.

Bacillus coli communis ferments glucose with production of a quantity of lactic acid corresponding to rather less than half the sugar, and of alcohol and acetic acid in approximately equivalent amounts, each representing about one-sixth of the carbon of the sugar. Small amounts of succinic and formic acids are also produced, and carbon dioxide and hydrogen evolved. The carbon dioxide amounts to 12—18 per cent of the sugar, whilst the volume of hydrogen is slightly greater. The lactic acid formed was found to be a mixture of inactive acid (25—5 per cent), with *l*-lactic acid (75—95 per cent). *B. typhosus* produces the same products from glucose, except that it yields a large amount of formic acid (17 per cent) and no gas. Some of the abnormal forms of *B. coli communis* act in a similar manner on glucose, others produce the same substances but in entirely different proportions. *d*-Fructose yields the same products of fermentation by *B. coli communis* as glucose, and *l*-arabinose and *d*-galactose also yield *l*-lactic acid. Mannitol yields a much larger proportion of alcohol, 26—29 per cent, and a much smaller amount of lactic and acetic acids. The production of alcohol by this organism therefore appears to depend on the presence of the group $CH_2(OH)\cdot CH\cdot OH$ in the compound to be fermented; glycerol, which also contains this group, yields nearly half its weight of alcohol when fermented by the same organism.

Formic acid is decomposed into carbon dioxide and hydrogen (Pakes and Jollyman), but lactic acid is not attacked, and hence the active lactic acid is probably not

produced by the selective decomposition of previously formed inactive acid.

When asparaginic acid is the sole nitrogenous nourishment, glucose and mannitol are fermented as usual by this organism, but a large proportion of the hydrogen is absorbed, and reduces the asparaginic acid to ammonium succinate.

DISCUSSION.

Mr. PAKES remarked with regard to the fact that Dr. Harden's experiments were made under anaerobic conditions, that quite different decompositions took place when the conditions were altered; for example, when nitrates were present with *d*-glucose, nitrogen was evolved instead of hydrogen; the yield of lactic and acetic acids was quite altered if the medium containing *d* glucose had abundant oxygen either free or in the form of nitrates. Again, out of 84 strains of typical *B. coli communis* under observation at the present time, about two-thirds inverted sucrose and subsequently fermented it, the remainder failing to invert it, did not ferment it; a similar selective power was noticed in the case of glycerin. Some, again, did not appear to be able to start the fermentation of glycerin under anaerobic conditions, but if the process were started, it would then continue anaerobically. He had observed a similar reaction with the *B. fluorescens liquefacians* in media containing nitrates; the bacilus would not begin to grow in this medium under anaerobic conditions, but if the growth were started by the introduction of a few cubic centimetres of oxygen, the decomposition of the nitrate would continue under strictly anaerobic conditions.

Dr. HARDEN, in reply, stated that the products of fermentation, in the presence and absence of oxygen, had frequently been found to be different. Anaerobic conditions seemed likely to furnish the most interesting results. The reduction of nitrates by this organism in presence of glucose appeared to be a secondary reaction of the same order as the reduction of asparaginic acid. The variability of the action of the organism on cane-sugar had been previously observed by Cushing, who, however, had not investigated the interesting question as to the inversion of the sugar by this organism.

*43. "*Action of Dry Silver Oxide and Ethyl Iodide on Benzoylacetic Ester, Deoxybenzoin, and Benzyl Cyanide.*" By G. D. LANDER, D.Sc.

The author has studied the action of silver oxide and ethyl iodide on benzoylacetic ester, deoxybenzoin and benzyl cyanide, as further examples of compounds analogous to acetoacetic ester (*Trans.*, 1900, lxxvii. 729).

With benzoylacetic ester either at the temperature of the steam-bath or in the cold, the course of the reaction is entirely similar to that of acetoacetic ester, the alkylated product consisting almost entirely of C-ethyl homologue, mixed, however, with minute quantities of β-ethoxycinnamic ester (Claisen, *Ber*, 1896, xxix., 1006). These substances were identified by dilute alkali hydrolysis, when phenyl propyl ketone, giving an oxime, m. p. 55—56° (*N* = 8·94 instead of 8·59 per cent), was obtained. The alkaline hydrolysis liquid yielded small quantities of β-ethoxycinnamic acid, separating by slow crystallisation from dilute alcohol in prisms, by more rapid re-crystallisation in leaflets melting at 160·5° with energetic evolution of gas, Claisen (*loc. cit.*) gives m. p. 162°; the isomeric ethylbenzoylacetic acid melts at 116°.

Only oxidation products were obtained from deoxybenzoin and benzyl cyanide.

After boiling deoxybenzoin for eight hours with silver oxide and ethyl iodide an unchanged substance and a minute quantity of a compound (m. p. 245°), sparingly soluble in alcohol, alone resulted. This latter compound was evidently bidesyl (m. p. 255°).

By the action of silver oxide on benzyl cyanide, either in the presence of ethyl iodide on the steam-bath, or in the absence of iodide in the cold, profound decomposition ensued. By rapidly heating the thick tarry product in a vacuum small distillates of dicyanostilbene were obtained (m. p. 158—159°), which gave the characteristic fluorescent green prisms of diphenylmaleic anhydride (m. p. 155°) on hydrolysis with alcoholic potash.

*44. "*Alkylation of Acylarylamines.*" By G. D. LANDER, D.Sc.

The alkylation of various acylarylamines, containing the aceto-, benzo-, oxalyl-, and oxal-residues, by means of dry silver oxide and alkyl iodides has been studied.

By means of oxide and ethyl iodide, O- or imino-ethers alone result, whereas when methyl iodide is employed the alkylation usually gives a mixture of N-, or acylalkylamine, and O- or imino-homologues. Apparently the methylation of acet-*p*-toluide yields N-ether alone. A partial explanation of this anomalous action of methyl iodide is afforded by the observation that simple heating serves to convert N phenylacetiminomethyl ether, $C_6H_5N\,C(OCH_3)CH_3$, into the N-substituted isomer.

The imino-ethers corresponding to acylarylamines are readily distinguished from the isomeric N-substituted compounds; by their liquidity at the ordinary temperature; by their boiling-points, which are from 30—50° lower than those of the acylalkylamines; by the characteristic behaviour on heating of their hydrochlorides when obtainable), regenerating acylarylamine by loss of alkyl chloride, and by their very ready hydrolysis by dilute hydrochloric acid into the original amine, acid, and alcohol. The presence of a methyl group in the ortho-position in the N-*o*-tolyl imino-ethers, however, inhibits this characteristic hydrolysis, it being possible to prepare platinichlorides of these ethers from aqueous solutions. N-α-Naphthylacetimino-ethyl ether seems also to possess greater relative stability than the β-naphthylisomer.

The following compounds have been obtained:—From acetylarylamines: N-*phenylacetiminomethyl ether* (with N-isomer), b. p. 197°; N-*o-tolylacetiminoethyl ether*, b. p. 222°, *hydrochloride*, m. p. 90—91° (with regeneration of acetotoluide), *platinichloride*, m. p. 171°; N-*o-tolylacetiminomethyl ether* (along with N-isomer), b. p. 212° (atmos.), *hydrochloride*, m. p. 79—80°, *platinichloride*, m. p. 169°; N-*p-tolylacetiminoethyl ether*, b. p. 232° (hydrochloride unstable); N-*α-naphthylacetiminoethyl ether*, b. p. 175° (12 m.m.), *hydrochloride*, m. p. 111°; N-*β-naphthylacetiminoethyl ether*, b. p. 176·5° (12 m.m.). From benzanilide: N-*phenylbenziminoethyl ether*, formerly prepared by Lossen (*Ann.*, 1891, cclxv., 138), b. p. 176° (12 m.m. From oxanilic ester, *semi-N-phenylimino-oxalic diethyl ether*, $C_6H_5N{:}C(OC_2H_5){\cdot}CO_2C_2H_5$. The dimethyl ether has been described by Anschütz and Stiepel (*Ber.*, 1895, xxviii., 61). The diethyl ether is a liquid, b. p. 152—155° (12 m.m.), decomposed by dry hydrochloric acid apparently into a mixture of oxanilic ester and anhydrous oxanilic acid; with aniline at 100° it gives *diphenylamidinooxalic ester*,—

$$C_6H_5N{:}C_6H_5NH{\cdot}C{\cdot}CO_2C_2H_5,$$

m. p. 73—74·5°, a base giving a stable platinichloride, and passing by warming with aniline at 160—170° into *diphenylamidino-oxalanilide*, melting when rapidly heating at 140—142°, softening at 134°.

From oxanilide: *di-N-phenylimino-oxalic diethyl ether*, $\{C_6H_5N{:}C(OC_2H_5)\}_2$, a viscid, brown, rather unstable oil, b. p. 205° (12 m.m.).

*45. "*The Preparation of Aliphatic Imino-ethers from Amides.*" By G. D. LANDER, D.Sc.

The synthesis of imino-ethers from acid amides has only been found possible hitherto with certain aromatic amides which give stable silver salts (Tafel and Enoch, *Ber.*, 1890, xxiii., 103). The same authors, in a later paper (*loc. cit.*, 1550), describe unsuccessful attempts to effect the analogous synthesis from some aliphatic amides.

The author has examined the possibility of accomplishing this by the aid of dry silver oxide and ethyl iodide.

Semi-imino-oxalic diethyl ether, $NH{:}C(OEt){\cdot}CO_2Et$ (compare Nef, *Ann.*, 1895, cclxxxvii., 288), boiling at

75—77° at about 20 m.m., can be readily prepared from ethyl oxamate by means of silver oxide and ethyl iodide at 100°. When urethane is warmed with ethyl iodide and silver oxide, there occurs a vigorous reaction, a liquid boiling from 90—200°, along with small quantities of triethyl isocyanurate, m. p. 93—94°, being obtained. The liquid is probably a mixture of ethyl iminocarbonate, unchanged urethane, and triethyl cyanurate.

The formation of imino-carbonic diethyl ether can be demonstrated by carrying out the reaction in the cold, separating the imino-ether from unaltered urethane by distillation below 85° (20 m.m.), purification by means of potassium hydroxide and conversion by hypobromite into brominocarbonic diethyl ether m. p. 40—42°, 0·4 grm. being thus obtained from 18 grms. of urethane.

The results of several experiments with acetamide, silver oxide, and ethyl iodide, carried out either at 100° or in the cold, unfortunately still leave the question of the formation of acetiminoethyl ether by this process open. The production of a liquid base of "imino" odour, volatile between 70° and 100°, from which, however, so far, only an oily hydrochloride has been prepared, nevertheless inclines the author to suppose that acetiminoethyl ether is actually one of the products of the reaction.

46. "*Note on the Latent Heats of Evaporation of Liquids.*" By H. Crompton.

Imagine a saturated vapour in so attenuated a state that the gas law $PV = RT$ applies to it. Assume that it were possible at constant temperature and by compression alone to reduce the volume of the vapour V_0 to the volume which the liquid it forms would normally occupy v_0, *without any change in state occurring, and the substance during this compression continuing to obey the gas law.* The work done in bringing about this change in volume would be—

$$\int_{v_0}^{V_0} p\,dv = \int_{v_0}^{V_0} \frac{RT}{v}\,dv = RT \log_e V_0/v_0;$$

and, as no change in temperature occurs, heat equivalent to this work will be given out during compression.

The vapour now occupies the volume of the liquid, but it is not yet liquid. It is by assumption a gas under high pressure, and if the pressure is now reduced to its original amount, the gas would expand to its original volume. To form the liquid the substance must be brought to such a state that it would be possible to reduce the pressure to the normal vapour-pressure of the liquid, without any corresponding change in volume. Assuming that no change in molecular aggregation occurs, the substance must then be deprived of the potential energy of expansion of the gas; that is, of the energy that would enable the molecules of the substance to occupy their original volume on a return to the original pressure. This energy is equal to that expended in compressing the material, namely, $RT \log_e V_0/v_0$. If this is removed in the form of heat, the total heat given out during the production of the liquid from the vapour is $2RT \log_e V_0/v_0$, and this is the latent heat of evaporation.

If, in the above, V_0 and v_0 apply to the grm.-molecule, R would have the value 1·976 calories, and $2RT \log_e V_0/v_0$ would be the molecular heat of evaporation. Dividing this by the molecular weight M, the latent heat of evaporation would be obtained in the ordinary units.

The observations of Cailletet and Mathias, with carbon dioxide, nitrous oxide, and sulphur dioxide, allow the above formula to be tested for fairly wide variations in temperature and pressure. D_0 is the density of the vapour, d_0 the density of the liquid, l the latent heat of evaporation. The calculated values are obtained by the method described. (See Table, next column).

In calculating the latent heats of evaporation at the ordinary boiling-points of liquids, we have approximately $V_0/v_0 = 22320 T d_0/273 M$, if d_0 is the density of the liquid at its boiling-point. In general, the calculated values are found to be about 5 to 10 per cent higher than the observed. This may be attributed to the fact that the saturated vapour at the boiling-point is not a perfect gas, and has usually a slightly higher density than that corresponding to the normal molecular weight M. With a few associating liquids, notably the alkyl alcohols, the calculated values are somewhat lower than the observed. Here, in addition to the changes described and accounted for, the production of molecular aggregates occurs on liquefaction, doubtless involving the evolution of heat. Hence the observed latent heat is higher than the calculated by this amount.

	T.	D_0.	d_0.	M.	l obs.	l cal.
Carbon dioxide	248	0·044	1·110	44	72·23	71·91
,, ,,	273	0·099	0·905	44	57·48	54·26
,, ,,	295·04	0·233	0·720	44	31·80	31·06
Nitrous oxide .	253	0·044	0·998	44	66·90	70·93
,, ,,	273	0·081	0·890	44	59·50	58·77
,, ,,	293	0·151	0·755	44	43·25	42·36
Sulphur dioxide	273	0·0045	1·4338	64	91·2	97·17
,, ,,	303	0·0136	1·3520	64	80·5	86·05
,, ,,	335	0·0364	1·2425	64	68·4	70·03

From the equation $l = 2RT(\log_e V_0 - \log_e v_0)/M$ we get $Ml/T = 2R(\log_e V_0 - \log_e v_0)$. According to the law of Trouton, Ml/T is approximately constant for liquids at their normal boiling-points, and has an average value of about 21. It will be found that for most liquids V_0/v_0 varies from 300 to 400. This gives a value varying from 22·8 to 23·9 for Ml/T. As, strictly speaking, in Trouton's formula M is double the vapour-density and not merely the theoretical molecular weight, slight abnormalities in the densities of the saturated vapours may account for the difference. As is well known, the boiling-points are approximately comparable points in the case of liquids. If liquids were truly comparable at the boiling-point, the ratio V_0/v_0 would be the same for all liquids at this point. Trouton's law according to the above expression would then hold absolutely.

(To be continued).

NOTICES OF BOOKS.

Traité Général des Applications de la Chimie. Par Jules Garcon. Tome premier, *Métalloïdes et composés Métalliques.* Paris: Dunod, Editeur. 1901. Pp. xxxviii.—747. Roy. 8vo.

This comprehensive treatise on the applications of chemistry reflects the tireless energy of the author previously shown in his three volume work on Dyeing ("La Pratique du Teinturier," 1893—97), and in his profound studies in bibliography ("Les Sources Bibliographiques des Sciences Chimiques," 1899, and "La Bibliographie Industrielles," 1901). The author's familiarity with cataloguing and indexing has enabled him to supply the work with bibliographical helps of importance and utility; this is shown in the arrangement of the volume, which contains a systematic table of contents, an alphabetical subject-index, a list of authorities consulted, besides a very full chapter on the sources of chemical bibliography (pages 1—29). It is gratifying to residents of the United States of America to notice that their country is foremost in the production of general and special bibliographies of chemistry.

Preliminary to the main subject three sections are devoted to important matters bearing on industrial chemistry:—First, the laws relating to patents in France; second, the laws of France concerning the conduct of manufactories using or producing dangerous and unsanitary bodies; this chapter has a table giving in alphabetical order the substances and the operations in the several classes under legal control; and thirdly, the laws of France regulating the transportation by railway, &c., of combustibles, explosives, infectious and other dangerous commodities.

The fifteen chapters of this volume assume knowledge of elementary facts and principles, and give under each of the non-metallic substances its uses in pharmacy, photography, dyeing, and technology. Under each non-metal is grouped the compounds of that body with metals instead of the reverse and more common way. This brings the potashes of commerce under carbon monoxide, the sulphides of arsenic, and of antimony under sulphur, and the use of dichromates in dyeing and printing under compounds of oxygen, in place of derivatives of chromium; this arrangement is, however, made clear by the alphabetical index.

We notice with regret rather favourable comments on the absurd claim of an American to the discovery of a method for transmuting silver into gold (p. 4), and a record of Fittica's conversion of phosphorus into arsenic (p. 633). We call attention also to the suggestive bibliography of water from the industrial point of view on pages 384 to 399.

The succeeding volumes will be awaited with interest, and if the elaborate programme of Vol. I. is carried out they will contain an immense amount of information not readily found elsewhere. Vol. I. has approximately the enormous number of 373,000 words. H. C. B.

CORRESPONDENCE.

ESTIMATION OF CARBOLIC ACID IN SOAP.

To the Editor of the Chemical News.

SIR,—Having frequently to estimate the carbolic acid in soap, and finding the following gives good results (compared with other methods), I venture to suggest that it may be useful to other analysts:—

20 grms. of the soap are boiled with 150 c.c. water and sufficient caustic soda to effect solution of soap. Excess of salt is then added, and the resulting lye poured on a filter. The soap is washed again with 75 c.c. saturated solution of brine, and the whole put on the filter. The filtrate is then treated in the usual manner with concentrated H_2SO_4. Two grms. stearic acid are then added to the hot filtrate. This melts and mixes with the carbolic acid. Cool, and remove the solid cake, which consists of stearic acid, plus carbolic acid. Weigh, and the weight less 2 grms. equals carbolic acid present in 20 grms. soap.

The cake will have a little moisture adhering to it, but may be removed with filter-paper.—I am, &c.,

J. J. PICKTHALL.

12, York Road, Knox Road,
Forest Gate, London, E.,
April 15, 1901.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxii., No. 12, March 25, 1901.

Electro-chemical Relations between the Allotropic Forms of Metals, particularly Silver.—M. Berthelot.—Owing to the evolution of sensible quantities of heat during the transformation of metals from one allotropic form to another, the author puts forward the theory of the possibility of developing an electric current between the two forms. This possibility was proved to be true in the case of silver, by using electrodes made of two of the allotropic forms of this metal, immersed in a solution of silver nitrate at a constant temperature, communication between the electrodes being made by means of a pure silver thread through a very sensitive Arsonval galvanometer. A current is immediately produced, the surface of the two specimens of silver tending to become identical.

Secondary Radio-activity.—Henri Becquerel.—Secondary radio-activity consists of (1) a portion not deviable by a magnetic field and easily absorbed; (2) a portion deviable by a magnet, which is apparently identical with cathode rays; and (3) a portion not deviable by a magnetic field and very penetrating. The present paper gives an account of researches on these three varieties of secondary radiation, to find whether they all give further secondary rays and whether the nature of these depends on that of the exciting rays. The experiments on these various points do not give a complete solution of the questions, but bring to light a number of interesting facts.

New Derivatives of Dimethylamidobenzoylbenzoic Acid.—A. Haller and A. Guyot.—When dimethylamidobenzoylbenzoic acid undergoes nitration by means of potassium nitrate and strong sulphuric acid, nitro-dimethylamidobenzoylbenzoic acid results:—

$$C_6H_4\begin{matrix}COC_6H_3\\CO\ OH\end{matrix}\!\!<\!\!\begin{matrix}N(CH_3)_2\\NO_2\end{matrix}+H_2O$$

From this is prepared the methylic ether and various other derivatives.

Specific Heat of a Gaseous Mixture of Bodies in Chemical Equilibrium.—A. Ponsot.—The system whose formation increases the volume of the mixture, and which displaces the other when the volume increases, is also that which tends to make up the gaseous mixture when the temperature rises beyond the limit, if the pressure remains constant or the volume is invariable. This formation increases the specific heat of the mixture and the increase is greater under constant pressure than under constant volume.

Induced Radio-activity in Gases due to Radium.—P. Curie and A. Debierne.—The authors have previously announced that induced radio-activity is not produced by direct rays from a radium salt, but that it is communicated by the air from molecule to molecule from the radium salt to the body which is exited. The present paper contains an account of researches on the precise part played by the gas in this phenomenon.

Method of Determination of Atomic Weights Founded on the Laws of the Transparence of Matter to X-Rays. Atomic Weight of Indium.—L. Benoist.—The specific opacity of a simple body, or that which practically represents this, its definite equivalent of transparence, constitutes a physico-chemical constant more closely allied to the atomic weight than specific heat, since it is independent of everything that makes the latter vary. The transparence of indium to X-rays, with all the variation in characteristics which accompany it, assigns to this simple body the atomic weight 113·4, to the formal exclusion of the value 75·6.

Action of Hydrogen on Realgar and the Inverse Reaction. Influence of Pressure and Temperature.—H. Pélabon.—When hydrogen acts on excess of realgar in a sealed tube, in presence of variable quantities of arsenic, it is observed that when the mass of this latter substance is above a certain limit, the proportion of sulphuretted hydrogen produced only depends on the temperature and remains constant, for the same temperature, if the relative proportions of realgar and arsenic are varied. The pressure of the gas exerts no influence on the limiting composition of the gaseous system.

Heat of Formation of Acetals compared with that of their Isomeric Compounds.—Marcel Delépine.—A comparison of the heats of formation of acetals with that of compounds isomeric in constitution and of different function leads to some interesting observations. It shows,

in a high degree, the thermic difference which exista between a body derived from a single carbon chain and s body derived from several carbon chains, re-united by oxygen and susceptible in general of decomposing by fixation of water. The present paper gives examples of ordinary ether compared with isobutylic alcohol and methyl formic ether compared with acetic acid, anisol, and *p*-cresylol.

Acidimetric Value of Mono-substituted Benzoic Acids.—G. Massol.—The author studies thermometrically the three oxybenzoic acids, the three nitrobenzoic acids, ortho-, chloro-, and iodo-benzoic acids, and *o*- and *p*-bromo-benzoic acids. For each of these he determines the heat of neutralisation by soda, the heat of solution of the anhydrous soda salt, and, for some acids, the heat of solution in water (at 15° when the solubility is great enough). In general, however, these acids are very slightly soluble in water. From these numbers he calculates the heats of formation of the anhydrous and solid soda salt direct from the solid elements. All the determinations are made under the same conditions of temperature and dilution; the heats of formation obtained compared with that of benzoate of soda. From these can be found the influence of an atom of chlorine, bromine, iodine, or of the substituted group OH or NO_2, and a thermometric measurement made of the increase in acidity of the molecule.

Passage of Anethol to Anisic Acid by Five successive Oxidations.—J. Bougault.—The table given below shows the various stages of the regular oxidation from anethol to anisic acid:—

Anethol	$CH_3O—C_6H_4—CH=CH—CH_3$.
By HgO and I ..	$CH_3O—C_6H_4—CH<^{CHO}_{CH_3}$.
By alkaline Ag_2O ..	$CH_3O—C_6H_4—CH<^{CO_2H}_{CH_3}$.
By chromo-sulphuric mixture	$CH_3O—C_6H_4—CO—CH_3$.
By alkaline MnO_4K	$CH_3O—C_6H_4—CO—CO_2H$.
By acid MnO_4K ..	$CH_3O—C_6H_4—CO_2H$ (anisic acid).

Naphthylol-naphthyl-oxy-naphthylmethane,—

$$OH—C_{10}H_6—CH<^{C_{10}H_6}_{C_{10}H_6}>O.$$

—R. Fosse.

Action of Zinc on the Dibromide and Di-iodide of Tetramethylene.—J. Hamonet.

MEETINGS FOR THE WEEK.

MONDAY, 22nd.—Society of Arts, 8. (Cantor Lectures). "Alloys," by Sir William Chandler Roberts-Austen, K.C.B., F.R.S.

TUESDAY, 23rd.—Royal Institution, 3. "On Cellular Physiology, with special reference to Enzymes and Ferments," by Allan Macfadyen, M.D., B.Sc.

WEDNESDAY, 24th.—Society of Arts, 8. "Patent Law Reform," by Alexander Siemens.

THURSDAY, 25th.—Royal Institution, 3. "Naturalism in Italian Painting," by Roger Fry.

FRIDAY, 26th.—Royal Institution, 9. "Colour in the Amphibia," by Hans Gadow, Ph.D., M.A., F.R.S.

—— Society of Arts, 8. (Howard Lectures). "Polyphase Electric Working," by Alfred C. Eborall, M.I.E.E.

—— Physical, 5. "On the Thermodynamical Correction of the Gas Thermometer," by Prof. Callendar, F.R.S. "On the Production of a Bright-line Spectrum by Anomalous Dispersion and its Application to the Flash Spectrum," by Prof. R. W. Wood.

SATURDAY, 27th.—Royal Institution, 3. "Climate, its Causes and Effects," by John Young Buchanan, M.A., F.R.S.

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THE CHEMICAL NEWS.

VOL. LXXXIII., No. 2161.

NOTE ON THE DETECTION AND ESTIMATION OF NITRIC ACID IN COMBINATION WITH THE ALKALI METALS.

By E. P. PERMAN, D.Sc.

THE author has observed, but has not seen anywhere recorded, that the nitrates of the alkali metals are decomposed if heated gently with the sulphate of any metal except those of the alkalis. The sulphate of the heavy metal is formed, and red fumes of nitrogen peroxide are evolved. This reaction may be used as a convenient dry test for a nitrate of the alkali metals; the substance is mixed with lead sulphate for example, or with ordinary alum (anhydrous), and heated, when red fumes will show the presence of the nitrate.

This method may also be applied quantitatively; the nitrate is heated with anhydrous potash alum, at first very gently, and finally to a low red heat for one or two minutes. If heated by the full flame of the Bunsen burner for any length of time, the aluminium sulphate will decompose, but the complete decomposition of the nitrate is effected before this takes place. The sulphate of the alkali metal remains together with alumina and the excess of the alum, and nitrogen peroxide and oxygen are expelled. From the loss of weight, which may be calculated as N_2O_5, the percentage of nitric acid in combination can be calculated. The author has obtained the following results: —

Percentage of NO_3 *in* KNO_3.

Found.	Calculated.
61·5	
61·2	61·4
61·3	

It is best to put the alum in the crucible first, and upon this the nitrate; the two need not be mixed if the quantity of nitrate is small (0·2 g. to 0·3 g.). The operation takes about ten minutes only, and the residue does not stick to the crucible.

Unfortunately the method is of no very general application, as the presence of a chloride causes the formation of the volatile aluminium chloride.

University College, Cardiff.
April 18, 1901.

THE ACTION OF WATER ON PENTACHLORIDE OF MOLYBDENUM.

By MARCEL GUICHARD.

WE will first set forth a few of the properties of the solution obtained by dissolving binoxide of molybdenum in hydrochloric acid; that is to say, the solution of the hydrated tetrachloride.

This solution is red when concentrated, and yellow when diluted; when very acid it is green, the addition of chloride of lime to the red solution changes it into a green solution; on the other hand, the green solution, diluted until it becomes red, changes to green when heated, and then becomes red again on cooling. Potash added to this solution of tetrachloride gives a red precipitate of hydrated binoxide. The variations of colour point to the existence of several hydrates of the pentachloride.

Finally, if we dilute a solution of the tetrachloride with water, it gradually becomes blue when exposed to the air.

We will now show what has been observed with regard to the action of water on pentachloride of molybdenum prepared by the direct combination of chlorine and molybdenum.

If we drop some anhydrous pentachloride of molybdenum into water a great deal of heat is given off, so that the solution appears to boil, though no gas is actually evolved. The solution obtained is red, and after dilution turns blue when exposed to the air. With the alkalis it gives a red precipitate of binoxide, and molybdic acid remains in solution. When hydrochloric acid or chloride of calcium are added the solution becomes green. In fact, the liquid resulting from the action of water on the pentachloride has all the characteristics of a solution of the tetrachloride. Berzelius (*Pogg. Ann.*, vi., p. 341), and Blomstrand (*Journ. f. Prakt. Chem.*, lxxi., p. 449; lxxvii., p. 88), found the formula $MoCl_4$ for the anhydrous chloride resulting from the action of chlorine on the metal: but since the research of Debray (*Comptes Rendus*, lxvi., p. 722), and those of Liecht and Kempe (*Liebig's Ann.*, clxi., p. 344), it is well-established that this compound is the pentachloride $MoCl_5$. It must be therefore admitted that the action of water on the pentachloride transforms it into the tetrachloride.

We have endeavoured to find out how this transformation is effected. In the first place, when it takes place there should be liberation of chlorine, but we have observed that the chlorine oxidises the tetrachloride, giving molybdic acid; the solution resulting from the action of water on pentachloride of molybdenum should therefore contain hydrated tetrachloride, hydrochloric acid, and free molybdic acid. The most simple equation by which this reaction can be represented is the following:—

$$2MoCl_5 + 3H_2O = MoCl_4 + MoO_3 + 6HCl.$$

We have confirmed this equation; in the first place, the solution is very acid, it gives a lively effervescence with marble; further, on the addition of an alkali it gives a precipitate of binoxide (by its action on the tetrachloride), only after a certain quantity has been added which corresponds precisely to the presence of free acids.

Again, if we react with the pentachloride, not on water, but on very concentrated hydrochloric acid, the reaction is the same, but the hydrochloric acid formed during the reaction is unable to dissolve, and is therefore given off in the gaseous state.

We have endeavoured to confirm this reaction quantitatively by titrating the free acids. To the fresh solution of the pentachloride in water we gradually added a titrated solution of potash. This potash first saturates the hydrochloric acid and the free molybdic acid, and then acts on the tetrachloride, giving a precipitate of hydrated binoxide. The appearance of the precipitate indicates the end of the saturation of the free acids. There is, however, some uncertainty as to the commencement of the precipitation; we therefore only give the following figures as being approximately correct.

0·1 grm. of $MoCl_5$ dissolved in water gave an acid solution which required, according to the above equation, 9·5 c.c. of the alkaline liquor used to bring about the commencement of the precipitation (found, 8·3 c.c., 8·0 c.c. 9·3 c.c.). The weights of pentachloride were calculated from the weight of the total molybdenum. The action of water on the pentachloride does not appear to be limited; it is complete immediately, and even with water saturated with hydrochloric acid gas it still takes place, since in this case we observe the disengagement of gas, and the formation of dissolved tetrachloride, which is green on account of the excess of oxide.

Thus the action of water on pentachloride of molybdenum gives rise to a mixture, in solution, of tetrachloride, molybdic acid, and hydrochloric acid.

We will now describe our research on the change undergone by this solution of pentachloride in water, when it is diluted. We must first remark that the solution only becomes blue on exposure to the air; titrations with permanganate show that the proportion of oxygen to metal

increases in a solution which becomes blue, a dilute solution obtained by the action of water on the pentachloride gives:—Mo, 70·05; O, 29·94. Calculated for Mo_2O_5, Mo, 70·58; and O, 29·41.

This solution after having turned blue on contact with the air gave:—Mo, 67·74: O, 32·26. Calculated for $MoO_2.4MoO_3$, Mo, 68·18 and O, 31·81.

There is thus an oxidation taking place, and this oxidation evidently forms $MoO_2.4MoO_3$; that is to say, the blue oxide. We can even demonstrate that the completely oxidised solution is nothing else than a solution of the pure blue oxide.

If we evaporate down a solution which has become blue after dilution and oxidation, we obtain a blue residue which is analogous to the molybdate from the binoxide, but it contains a little chlorine; if we re-dissolve it in water it gives a deep blue solution, which, when again evaporated down on the water-bath, still contains a little chlorine. After several successive evaporations and re-solutions, we eventually obtain a blue substance which does not contain a trace of chlorine, and which on analysis gives results very close to those required by the formula $MoO_2.4MoO_3$. Mo in the supposed anhydrous oxide = 67·52, 67·35, 67·63; calculated 68·18.

These figures are, as a matter of fact, too low, as the blue oxide is itself slowly oxidisable. If we turn to what we pointed out in our research on the blue oxide (*Bull. Soc. Chim.*, 1901), we are able to explain the mechanism of the change which takes place in a solution obtained by the action of water on the pentachloride.

We have said that this solution, at the moment of being made, contains one molecule of molybdic acid for one molecule of binoxide in the form of tetrachloride; it cannot therefore form the blue oxide which contains four molecules of molybdic acid for one of binoxide except by becoming oxidised. By oxidation a part of the binoxide it contains is transformed into molybdic acid, and, if the solution is diluted with water, this molybdic acid displaces the hydrochloric acid, as we have shown, when the acidity becomes sufficiently low to permit the existence of the blue molybdate.

After several evaporations the whole of the hydrochloric acid set free has disappeared. A concentrated solution will never become blue, as it is too acid.

The transformation of the red solution into the solution of blue oxide thus takes place in two phases:—1. Oxidation of a part of the binoxide it contains. 2. Displacement of the hydrochloric acid by the molybdic acid formed.

To sum up, after examining the action of water on the pentachloride of molybdenum we have come to the conclusion that this chloride cannot exist in solution; it is decomposed and transformed into tetrachloride, molybdic acid, and hydrochloric acid. Finally, the solution obtained is transformed by the oxidising action of the air into the blue oxide, and this reaction would afford a means of preparing the blue oxide, if this compound were not itself slowly oxidisable.—*Bull. Soc. Chim.*, Series 3, vol. xxv., No. 4.

Northern Polytechnic Institute.—The Governors of this Institution have appointed Mr. R. T. Smith, B.A. (Cantab.), as Principal of the Institute, in succession to Dr. Dunn, who is leaving to take up practice as an Analytical and Consulting Chemist in the North of England. Mr. Smith was 34th Wrangler in his year, and afterwards took a Second Class in Part II. of the Natural Science Tripos. He organised and equipped the South African College at Cape Town, and acted as Professor of Mathematics and Physics in the College for some years. Returning to England he took up work with Messrs. Vickers, Son, and Maxim, and was also appointed Lecturer in Mathematics and Physics in the Goldsmiths' Institute, New Cross. The new Principal will undertake the teaching of Mathematics in the Northern Polytechnic Institute.

THE MOLECULAR WEIGHT OF ALUMINIUM COMPOUNDS.*

By ELMER P. KOHLER.

THE molecular weight of aluminium compounds has been the subject of investigations by—

Deville and Troost	*Ann. Chim. Phys.*, [3], lviii., 257.
Odling and Buckton	*Phil. Mag.*, [4], xxix., 316.
V. Meyer and C. Meyer ..	*Ber. d. Deut. Chem. Gesell.*, xii., 1199.
Nilson and Pettersson ..	*Zeit. Phys. Chem.*, i., 456.
Friedel and Crafts	*Comptes Rendus*, cvi., 73; cvi., 602; cvii., 600.
Roux and Louise	*Comptes Rendus*, cvi., 1764.
Combes..	*Comptes Rendus*, cviii., 405.
Werner and Schmujlow ..	*Zeit. Anorg. Chem.*, xv., 24.

All of the earlier results, obtained by applying vapour-density methods to aluminium halides, lead to the general formula Al_2X_6 for these salts. All the later results—obtained partly by vapour-density and partly by newer methods—lead to the general formula AlX_3 for all classes of aluminium compounds. The last two investigations, in particular, have appeared so conclusive that the double formulæ have been more or less reluctantly abandoned. Combes determined the vapour-density of aluminium acetylacetone and obtained results that agree perfectly with the formula $Al(C_5H_7O_2)_3$, showing that in compounds of this type aluminium is unquestionably trivalent. Werner and Schmujlow determined the molecular weight of aluminium chloride by the boiling-point method, using pyridine as solvent. Their results agree closely with the formula $AlCl_3$.

The investigation described in this paper was undertaken as the result of some observations made while studying the mechanism of organic reactions that are induced by aluminium halides. The aim was the determination of the molecular weight of aluminium halides, as well as that of their addition- and reaction-products, as nearly as possible under the same conditions as those under which they are used and formed in organic reactions; namely, dissolved in some low-boiling, indifferent medium.

The substances studied were:—

I. Organic compounds, like aluminium acetylacetone.
II. Aluminium halides.
III. Compounds formed by the addition of aluminium halides to a number of different classes of organic and inorganic compounds.

Nearly all the determinations were made by the boiling-point method, with carbon disulphide as solvent; but at the end of the paper some experiments are described in which nitrobenzene was used as solvent for determinations by the freezing-point method. These were made to determine the behaviour of the addition-products above referred to in the presence of a large excess of one of the components. They show the relation between the results described in this paper and those obtained by Werner and Schmujlow.

I. Organic Aluminium Compounds.

Aluminium Acetylacetone.

Solvent: Carbon disulphide. K = 2370.

	Solvent. Grms.	Substance. Grms.	Rise in boiling-point.	Molecular weight.
1.	39·4195	1·2340	0·194	329
2.	39·4195	1·7848	0·330	326
3.	39·4195	2·3458	0·425	331
	Mean			328
	Calculated for $Al(C_5H_7O_2)_3$ ..			324·3

* From the *American Chemical Journal*, xxiv., No. 5.

Aluminium Acetoacetic Ester.

Solvent: Carbon disulphide. K = 2370.

	Solvent. Grms.	Substance. Grms.	Rise in boiling-point.	Molecular weight.
1.	40·1505	1·5400	0·220	413
2.	40·1505	2·1825	0·306	421
3.	40·1505	2·8050	0·396	418
		Mean..		417
		Calculated for $Al(C_6H_9O_3)_3$..		414·4

These determinations presented no difficulties, and the results, as expected, fully confirm those of Combes.

II. ALUMINIUM HALIDES.

Aluminium chloride is insoluble in carbon disulphide, hence its molecular weight could not be determined directly. An indirect determination is given under the addition-products.

Aluminium bromide was made by Mallet's method (*Trans. Roy. Soc.*, 1880, 1003; and *Am. Chem. Journ.*, iii., 77), from pure bromine and metallic aluminium. To avoid the troublesome distillations necessary to free it from bromides of carbon, silicon, and iron, the following method of purification was adopted:—A piece of Jena glass tubing 3 metres long was constricted at three points, and bent, at the constrictions, into a flattened W. One of the ends was drawn into a capillary and connected with a phosphorus pentoxide drying-tube, which, in turn, was connected with a pump. Aluminium wire that had been heated to a low red heat in a current of hydrogen was placed in the limb next to the other end, that connected with the retort in which the bromide had been prepared, and the latter distilled into the tube. This end of the tube was then sealed off. The limb holding the bromide and wire was wrapped with thin asbestos paper and placed in a furnace in such a position that the second limb served as a reflux condenser. The bromide was boiled until colourless, when the other end of the tube was sealed off, the position of the tube changed, and the bromide distilled from the first into the second limb. The first limb was then sealed off at the constriction, the position of the tube changed, and the distillation repeated, &c. The second distillation left a slight residue of oxybromide; the third, no residue at all. The bromide was thus obtained sealed up in the fourth limb. To get it into convenient form for use, it was melted into a layer of uniform thickness throughout the length of the tube. By hitting the tube sharply with a block of wood, the layer could be readily broken up into lumps of any desired size. In this way there is no difficulty either in preparing or manipulating the bromide.

The principal difficulty met with in this part of the work consisted in getting and keeping carbon disulphide sufficiently free from water. After a most careful purification it was repeatedly distilled from phosphorus pentoxide; but though used immediately after distillation, enough water was invariably present to cause errors of from 50 to 100 in the molecular weight. The difficulty which has been experienced by others (Rosenheim and Woge, *Zeit. Anorg. Chem.*, xv., 283) working with such sensitive substances, is due to the adsorption of water by the apparatus. To remove this water, the weighed molecular-weight apparatus was filled with dry carbon disulphide, and a considerable quantity of the latter distilled off, the vapour sweeping freely through the condenser. The condenser was then capped with phosphorus pentoxide tubes that were ground on, the apparatus closed with a ground-glass stopper, and weighed with the thermometer in place.

Pure dry carbon disulphide dissolves aluminium bromide without any indication of chemical action. The solution is clear and colourless; its boiling-point remains constant during protracted boiling; and, if the disulphide is allowed to evaporate at ordinary temperatures, the pure bromide crystallises out in large lustrous rhombohedra. These are far less sensitive to atmospheric moisture than the lumps of the fused salt. An analysis of the crystals gave 10·02 per cent aluminium and 89·72 per cent bromine, instead of the calculated 10·15 per cent aluminium and 89·85 per cent bromine.

Molecular Weight of Aluminium Bromide.

Solvent: Carbon disulphide. K = 2370.

	Solvent. Grms.	Substance. Grms.	Rise in boiling-point.	Molecular weight.
1.	40·1510	0·6110	0·067	539
2.	40·1510	1·3660	0·149	542
3.	40·1510	2·2895	0·250	540
4.	40·1510	3·1000	0·340	538
5.	40·1510	3·7410	0·405	545
6.	40·1510	4·3840	0·479	540
		Mean..		540·6
		Calculated for Al_2Br_6		534

Aluminium Iodide.

The iodide was prepared by the method of Gustavson (*Liebig's Ann. Chem.*, clxxii., 173), and purified in exactly the same way as the bromide.

Solvent: Carbon disulphide. K = 2370.

	Solvent. Grms.	Substance. Grms.	Rise in boiling-point.	Molecular weight.
1.	40·4550	1·0120	0·072	824
2.	40·4550	1·5175	0·110	808
3.	40·4550	2·2380	0·160	819
4.	40·4550	3·1080	0·222	822
5.	40·4550	4·3200	0·310	826
		Mean		822·25
		Calculated for Al_2I_6		815·30

(To be continued).

SOME PRINCIPLES AND METHODS OF ROCK ANALYSIS.*

By W. F. HILLEBRAND.

(Continued from p. 187).

XVII. *Chromium.*

IF vanadium is absent, or nearly so, as is apt to be the case in those highly magnesian rocks (peridotites) usually carrying a good deal of chromium, the following separation and gravimetric method for chromium gives good and concordant results, but in presence of vanadium, and it is best generally to assume its presence, the colorimetric method should always be adopted.

Gravimetric Method.

Having obtained chromium in solution as chromate and free from all else but a little alumina, as at the conclusion of the preceding section on phosphorus, proceed as follows:

Concentrate if necessary, and add fresh ammonium sulphide, or introduce hydrogen sulphide. The chromium is reduced and appears as a precipitate of sesquioxide mixed with the rest of the alumina. This precipitate is now treated according to Baubigny (*Bull. Soc. Chim.*, New Series, 1884, vol. xlii., p. 291; CHEMICAL NEWS, 1885, vol. l., p. 18), by dissolving in nitric acid, evaporating to near dryness, and heating with strong nitric acid and potassium chlorate, finally evaporating to dryness to get rid of the acid. Oxidation is complete and very speedy. On dilution with cold water, acid sodium carbonate is added in slight excess, and after two or three hours the precipitated alumina is filtered off. From the filtrate the chromium is then thrown out by fresh ammonium sulphide, re-dissolved and re-precipitated to free from alkali, and weighed.

The separation of aluminum from chromium by hydrogen peroxide in ammoniacal solution, as recommended by Jannasch and Cloedt (*Zeit. fur Anorg. Chemie*, 1895, vol. x., p. 402), has been shown by Friedheim and

* *Bulletin of the United States Geological Survey*, No. 176.

Brühl (*Zeit. fur Anal. Chemie*, 1899, vol. xxxviii., p. 681), together with most of the other separations of Jannasch based on the use of hydrogen peroxide, and from which so much was hoped, to be valueless.

Colorimetric Method.

For this very accurate and by far the quickest method* for determining chromium in rocks and ores where the amount does not exceed a few per cent, there is needed the aqueous extract of a sodium-carbonate fusion of the rock (as obtained, for instance, under "Phosphorus," p. 186), in order to compare its colour with that of a standard solution.

Preparation and Strength of Standard Solution.—This standard solution is made by dissolving 0·25525 grm. or double that amount of pure potassium monochromate in one litre of water made alkaline by a little sodium carbonate. Each cubic centimetre then corresponds to one-tenth m.grm. or two-tenths m.grm. of chromic oxide (Cr_2O_3), in which condition chromium is usually reported in rocks and ores. It is probably inadmissible to increase the strength of the standard much above the figure given.

Preparation of the Test Solution.—Before filtering the aqueous extract of the sodium-carbonate fusion a few drops of alcohol (ethyl or methyl) are added to destroy the colour of sodium manganate. If the yellow colour of the filtrate is very faint, concentration by evaporation will strengthen it, and less than 2 m.grms. of chromic oxide in 1 grm. of rock can then be exactly measured. For smaller amounts it is best to employ from 3 to 5 grms. of powder, and then to concentrate the chromium by precipitation by mercurous nitrate, as detailed in the next section under "Vanadium" (see *prox.*); otherwise it may be difficult or impossible, because of the large amount of alkali carbonate present, to obtain a filtrate of sufficiently small bulk to show a decided colour.

If nitre has been used in the fusion and the crucible has been at all attacked by it, a yellow colouration of the filtrate may be due to dissolved platinum, but neither the proportion of nitre nor the temperature of the blast should ever be high enough to permit the crucible to be attacked.

Comparison of Colours.—The final solution is transferred to a graduated flask of such size that its colour shall be weaker than that of the standard chromium solution. Definite amounts of the latter are then diluted with water from a burette until of the same strength as the test solution, exactly as described on page 177 for the colorimetric estimation of titanium. For very minute amounts it is necessary to use Nessler tubes, as in ammonia estimations, instead of the glasses and apparatus described and depicted under "Titanium" (p. 177).

As with colorimetric methods in general, this one gives better results with small than with large percentages of chromium, yet it can be applied in the latter cases with satisfactory results by making a larger number of consecutive comparisons with the same solution.

A few Comparative Data.

A few comparisons between colorimetric and gravimetric determinations of chromium are here given to show the order of agreement, the former having been made several months and even years after the latter.

TABLE IV.

Gravimetric per cent Cr_2O_3.	Colorimetric per cent Cr_2O_3.
Trace	0·018
0 05	0·051
0·14	0·12
0·08	0·083
Trace	0·013
None	0 0086
None	0·0067

* W. F. Hillebrand (*Journ. Am. Chem. Soc.*, 1898, vol. xx., p. 454; CHEMICAL NEWS, 1898, vol. lxxviii., pp. 227, 239; *Bull. U. S. Geol. Survey*, No. 167, p. 37). First applied by L. de Koningh ("Nederl. Tyds. voor Pharm. Chem. and Tox., 1889"), for the estimation of chromium in foodstuffs.

The outcome was somewhat surprising, for it was hardly to be expected that the long and laborious quantitative separations should have resulted so well as they are shown to have done. It should be mentioned that for the gravimetric tests but 1 or 2 grms. at most were used, which accounts for the reported absence of chromium in two instances, this report being based on the lack of colour in the aqueous extract of the alkali fusion after removal of manganese.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 21st, 1901.

Professor THORPE, C.B., F.R.S., President, in the Chair.

(Concluded from p. 190).

47. "*On the Atomic Weight of Lanthanum, and on the Error of the 'Sulphate Method' for the Determination of the 'Equivalent' of the Rare Earths.*" By BOHUSLAV BRAUNER and F. PAVLÍČEK.

Lanthanum material was prepared from crude cerite material and purified, first by repeated re-crystallisation of the double ammonium nitrate. The nitrate was then further purified by fusion with potassium sodium nitrate, traces of cerium, praseodymium, and yttrium being thus removed, after which the material was further fractionated by this process of fusion. The purest lanthanum nitrate was next subjected to a series of fractional precipitations with potassium hydroxide so that about 7/8 of the earth was precipitated, and the most "positive" fraction contained in the filtrate was converted into the pure oxalate and designated as La 1. In the same way, fractions La 2—La 7 were obtained, La 7 being most "negative" of the series. After this followed the still more negative fractions A1—A6, obtained by fusion with nitre.

For the determination of the atomic weight the oxide (from the oxalate) was converted into the sulphate, and the conditions accompanying its formation were carefully investigated. On heating the sulphate to a constant temperature of 450° and repeatedly weighing, a gradual decrease of weight was observed until at last an approximately constant weight was obtained corresponding to an atomic weight of about La=138. On heating the salt in an atmosphere of ammonium carbonate, further loss of sulphuric acid takes place, and an atomic weight of La=138·2 (O=16) was obtained with the purest material (La 1), a number which, owing to the condordant determinations of Brauner, Cleve, and Bettendorf, has hitherto been regarded as the true atomic weight of lanthanum. This number is, however, incorrect, a careful investigation having shown that the sulphate so obtained contains some of Wyrouboff's *acid sulphate*. This acid sulphate is so stable that even at temperatures above 500° some of it remains undecomposed, whilst another part of the sulphate, in the same crucible, may have undergone a partial decomposition into the basic sulphate. An aqueous solution of a sulphate so prepared shows, with ethyl orange as indicator, a strongly acid reaction, whereas the true normal sulphate obtained by repeated re-crystallisation is perfectly neutral towards ethyl orange. Every sulphate obtained in this way was therefore dissolved in water, tested with ethyl orange, and a *N*/20 solution of sodium hydroxide added until the red colour of the indicator was converted into the yellow tint shown by the normal neutral lanthanum sulphate solution containing ethyl orange. The error of the atomic weight of lanthanum due to the presence of sulphuric acid in the form of an acid sulphate may amount to −0·8 of a unit.

All "equivalent" determinations of the rare earths made

by the "sulphate method" during the 19th century are vitiated by this error. This error is largest with the most positive lanthanum, and diminishes as the basicity of the earth decreases.

After the determination and application of the above correction the single fractions of lanthanum gave the following atomic weights (means of several determinations):

La 1.	La 2.	La 3.	La 4.	La 5.	La 6.	La 7.	A 5+6.
138·78	138·80	138·88	138·97	138·98	139·07	139·10	139·25

The sulphate is very hygroscopic, and absorbs moisture during weighing. After excluding this error completely by means of a novel cooling and weighing arrangement, it was found that a correction of +0·2 to +0·3 must be applied to the whole series so that the atomic weight of the most positive fraction becomes La=139·0.

Lanthanum is a complex of two earth metals consisting, however, chiefly of the true lanthanum with the atomic weight La=139·0. Gibbs' and Shapleigh's results confirm this, for they found for the *mixture* the atomic weight 139·7.

48. "*On the Atomic Weight of Praseodymium.*" By B. Brauner.

The atomic weight of this element was determined by four methods. (1). By the analysis of the anhydrous sulphate. The oxide of the approximate formula, Pr_4O_7, remaining after strong calcination of the sulphate was analysed by Bunsen's iodometric method, and the weight of the pure Pr_2O_3 was determined; this series gave Pr=140·95. (2). By the analysis of the oxalate. The amount of pure Pr_2O_3 contained in the oxide Pr_4O_7, which remains after calcination, was determined as in (1), and the oxalic radicle was determined by a novel gravi-volumetric method with permanganate. A series of fractions was obtained by fusion of praseodymium nitrate with nitre, but all gave the same number, Pr=140·95, so that no decomposition into different earths took place. (3). By synthesis of the sulphate. A known quantity of the oxalate containing a known quantity of the oxide, Pr_2O_3, as determined in (1) and (2) was converted into the sulphate by the usual method. Different fractions did not show any sign of decomposition, but the atomic weight deduced in this way was lower than in (1) and (2), being only Pr=140·78. As in the case of lanthanum it was found that praseodymium sulphate also does not part completely with the slight excess of free sulphuric acid (acid sulphate of Wyrouboff) on heating, and therefore shows an acid reaction. Using a normal sulphate tinted with ethyl orange as indicator as the standard of comparison, this excess of sulphuric acid was determined with *N*/20 sodium hydroxide. The result of series (4), in which the error due to the hygroscopic nature of the oxide and of the anhydrous sulphate was eliminated, gave the atomic weight Pr=140·93. Excluding series (2) as it was vitiated by an error which became known only at a later period, and which caused Jones and v. Scheele to obtain the incorrect number Pr=140·4—140·5, the mean result is Pr=140·94.

The above results only prove that the equivalent of praseodymium is 47, so that the atomic weight is either $Pr^{I}=47$ or $Pr^{II}=94$, $Pr^{III}=141$, $Pr^{IV}=188$, or $Pr^{V}=235$. In order to solve this question the molecular weight of the anhydrous chloride was determined by the ebullioscopic method, absolute alcohol being used as the solvent. Several determinations gave numbers for the molecular weight approaching 247·4 (this corresponds to $PrCl_3$); so that this fact, together with the analogies pointed out three years ago (*Proc.*, 1898, xiv., 71), proves definitely that the true atomic weight of praseodymium is Pr=140·94.

49. "*On Praseodymium Tetroxide and Peroxide.*" By B. Brauner.

When the author published his preliminary note (*Proc.*, 1898, xiv., 71), he left unsolved many of the problems connected with the black higher oxide which he was the first to prove possessed the formula Pr_2O_4. This oxide was subjected to a new and careful investigation. The only method for obtaining this oxide pure is by fusion of the nitrate with nitre, the combustion of the oxalate employed by v. Scheele giving a very impure compound. The pure praseodymium tetroxide has a sp. gr. of 5·978 (at 20°/4° and in a vacuum); the pure trioxide, Pr_2O_3, has a sp. gr. of 7·068. The molecular volume of $Pr_2O_4=57·9$, that of $Pr_2O_3=46·7$, hence the volume of the active (the fourth) oxygen atom is +11·2, an unusually large number for the volume of 1 atom of active oxygen. Hence we can understand the great instability of the salts of the type PrX_4. The oxides, Pr_2O_4 and Pr_2O_3 combine to form a complex oxide of the approximate composition Pr_4O_7, or more correctly $Pr_{10}O_{18}$, of sp. gr. 6·704, showing that slight contraction has taken place. The *pure* praseodymium tetroxide does not give the hydrogen peroxide reaction, and is a purely *ozonic* oxide. It gives free chlorine with hydrochloric acid, ozonised oxygen with oxy-acids; in acid solution, it oxidises cerous salts to ceric salts, manganous salts to permanganic acid, and gives the characteristic violet colouration with a solution of strychnine in sulphuric acid. It "catalyses" with hydrogen peroxide in acid solution,

Praseodymium nitrate yields with hydrogen peroxide, with sodium peroxide and an alkali, the hydrated real peroxide, Pr_2O_5, belonging to the *antozonic* oxides. To the same type belongs the acetate the composition of which may be represented by the formula—

$$Ac_2{:}Pr^{III}{\cdot}O{\cdot}O{\cdot}O{\cdot}Pr^{III}{:}(OH)Ac+H_2O.$$

The maximum valency of praseodymium is tetrad, like that of cerium. The corresponding oxides have a smaller volume (greater density) than those of cerium, which it resembles most of all elements, but no place has been found in the periodic system for an element possessing the physical and chemical properties of praseodymium and its compounds.

50. "*Note on Neodymium.*" By B. Brauner.

Applying the "sulphate method" for the determination of the atomic weight of neodymium as in the case of lanthanum and praseodymium, the neodymium material, purified with sodium sulphate, gave the atomic weight Nd=143·80, the correction due to the presence of the acid sulphate being determined experimentally. Neodymium forms (in the dry way) a higher oxide, Nd_2O_4, with such an extremely feeble tension (potential) of the active (fourth) oxygen atom that on liberation with acids this oxygen passes through ferrous salt solutions without oxidising them. Many other rare earths will probably form higher oxides of the same type, but their preparation and investigation offer great difficulties. These acids seem to represent the extreme limit of *ozonic* oxides.

In addition to this, neodymium yields purely *antozonic* compounds of the type R_2O_5, like the hydrated peroxide and the peculiar acetate,—

$$Ac{:}Nd^{III}{\cdot}O{\cdot}O{\cdot}O{\cdot}Nd^{III}{:}(OH){\cdot}Ac+H_2O,$$

strictly analogous to the corresponding praseodymium compounds.

The difficulties of finding a place for neodymium in the periodic system are even greater than in the case of praseodymium.

51. "*Contribution to the Chemistry of Thorium.*" By B. Brauner.

The results obtained on studying the behaviour on hydrolysis of the salt, $Th(C_2O_4{\cdot}NH_4)_4+7H_2O$ (*Trans.*, 1898, lxxiii., 951), were applied to the fractionation and purification of commercial thorium compounds. In this way, at the one end of the series the most basic positive fractions were obtained, that is, those which are most easily hydrolysed and termed Th_α, and at the other the most acid negative fractions which are most easily hydrolysed, and which are called Th_β.

After removing the trivalent rare earths by methods indicated (*loc. cit.*), the atomic weight of thorium contained

in the most basic (positive) fractions was determined, and the numbers $Th_\alpha = 233{\cdot}5$ (by the oxalate method) and $Th_\alpha = 233{\cdot}3 - 233{\cdot}7$ (by the sulphate method) were found.

The most negative ($Th\beta$) fractions gave at first the atomic weight $Th\beta = 232{\cdot}5$, and this by further purification of the material decreased to $Th\beta = 232{\cdot}0$ and $231{\cdot}9$. By working up a much larger quantity of material and trying to determine the atomic weight by the oxalate method, abnormal results were obtained owing to the easy formation of basic salts by the $Th\beta$ material, a property not possessed by the ordinary thorium salts. An extremely careful set of analyses by the oxalate method gave $R^{IV} = 236{\cdot}3$, whereas an analysis of the sulphate precipitated by alcohol from an aqueous solution which must be strongly hydrolysed gave $R^{IV} = 280{\cdot}7$. Ordinary thorium sulphate, owing to only partial hydrolysis of the sulphate in the aqueous solution, gives under the same conditions of precipitation $R^{IV} = 234{\cdot}6$, that is, only a slightly basic salt.

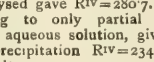
On further fractionation of the most negative ($Th\beta$) fraction, a material was obtained which, after conversion into the normal sulphate and its analysis, gave $Th\beta = 220$. This decrease of the atomic weight from 232 to 220 is accompanied by a decrease in the density of the oxide from 10·2 to 9·6 along with the property of the β-fractions of easily forming basic salts—a property exhibited by no known earth, with the exception of zirconium, which, however, cannot be present, may be regarded as proving the complex nature of thorium. These thoroughly established facts have been known to the author for years, but he abstains from further conclusions, especially as the study of the very complicated spectral phenomena connected with the above research proceeds but slowly.

52. "*Pheno-α-ketoheptamethylene and its Derivatives.*" By F. S. Kipping and A. E. Hunter.

The authors have continued the investigation of the ketone obtained by the action of aluminium chloride on phenylvaliric chloride (Kipping and Hall, *Proc.*, 1899, xv., 173), and have proved that it contains a seven carbon atom ring condensed with benzene in the ortho-position, as on oxidation with dilute nitric acid it yields *o*-phthalic acid.

Pheno-α-ketoheptamethylene oxime crystallises from dilute alcohol in lustrous needles melting at 108—109°; the corresponding phenylhydrazone and *p*-bromophenylhydrazone do not crystallise readily, and are oxidised on exposure to the air.

Pheno-α-aminoheptamethylene,—



is obtained when the oxime is reduced with sodium amalgam in acetic acid solution; it is a strongly basic, colourless liquid which absorbs carbon dioxide on exposure to the air.

The *hydrochloride*, $C_{11}H_{15}N,HCl$, is only moderately soluble in cold water, and crystallises in small prisms which do not melt at temperatures below 250°.

The *platinichloride*, $(C_{11}H_{15}N)_2,H_2PtCl_6$, forms orange needles. The *picrate* crystallises well, and is only sparingly soluble. The *sulphate* forms thin, transparent plates, and melts at about 229°; like the *oxalate*, it is only moderately soluble in water.

The *benzoyl* derivative crystallises in felted masses of needles melting at 171—172°.

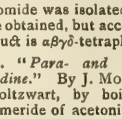
53. "*Note on Diphenyldinitroethylene.*" By J. J. Sudborough.

In the last number of the *Berichte* (1901, xxxiv., 619), Julius Schmidt describes two stereoisomeric *s*-diphenyldinitroethylenes, $NO_2{\cdot}CPh{:}CPh{\cdot}NO_2$, the one melting at 186—187°, and the other at 105—107°. Both compounds were obtained by the direct addition of nitrogen peroxide to tolane. The compound melting at 105—107° was prepared by the author several years ago (*Diss.*, 1893; *Trans.*, 1897, lxxi., 223; Richter's *Lexicon II.*, 1422), by the addition of nitrogen peroxide to monochlorostilbene, and the subsequent elimination of hydrogen chloride. The melting point was given as 104—105°, and it crystallised in sulphur-yellow prisms and pyramids resembling those described by Schmidt. The molecular weight was determined and the action of bromine investigated, but no dibromide was isolated, and no definite reduction products were obtained, but according to Schmidt the chief reduction product is $\alpha\beta\gamma\delta$-tetraphenyl piperazine.

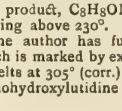
54. "*Para- and Ortho-cyanohydroxy-derivatives of Pyridine.*" By J. Moir, M.A., B.Sc.

Holtzwart, by boiling an aqueous solution of the polymeride of acetonitrile, $C_4H_6N_2$, obtained a condensation product, $C_8H_8ON_2$, which he described merely as melting above 230°.

The author has further investigated this substance, which is marked by extraordinary stability, and finds that it melts at 305° (corr.) and that it is, in all probability, a cyanohydroxylutidine of the constitution—



isomeric with the compound—



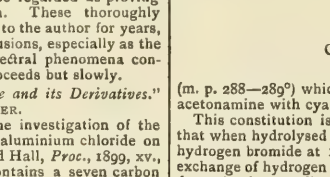
(m. p. 288—289°) which Guareschi obtained from acetylacetonamine with cyanoacetic ester.

This constitution is based on the fact, among others, that when hydrolysed by heating with strong solution of hydrogen bromide at 170°, it yields pseudolutidostyril, by exchange of hydrogen for cyanogen. All attempts to produce the intermediate carboxy-acid have failed. This acid has been obtained by Collie by an analogous reaction. Attempts to synthesise the cyano-compound from Collie's acid and ester have also been without result, owing to the stability of the compounds in question.

The mechanism of the condensation is evidently as follows:—

(1). $CH_3{\cdot}C(NH_2){:}CH{\cdot}CN + H_2O \rightarrow CH_3{\cdot}C(OH){:}CH{\cdot}CN$ (cyanoacetone).

(2).



The author has also found that the supposed third isomeride of $C_8H_8ON_2$, prepared by von Meyer from a compound, $C_8H_9N_3$, by the action of nitrous acid, is in reality identical with Holtzwart's isomeride. It follows that $C_8H_9N_3$ is 3-cyano-2:4-dimethyl-6-aminopyridine.

A careful physical and chemical comparison of Holtzwart's and Guareschi's isomerides has been made, and, although they resemble one another very closely, they were found to be different.

Both compounds form white, sparingly soluble needles of a very bitter taste; they are not basic, but form soluble derivatives with the alkali-metals, and cannot be directly methylated. Both resist hydrolysis with strong alkalis and acids, but give pseudolutidostyril with hydrogen bromide. They differ in their action on polarised light, and when mixed the melting-point is depressed. Different

compounds are obtained from each by bromination and nitration. The bromo-derivative of Holtzwart's isomeride melts at 307—308°; that of Guareschi's compound at 260—262°. The nitro-compound of Holtzwart's isomeride melts at 262° and forms yellow salts; that of Guareschi's compound melts at 271°, and forms white salts which give yellow solutions. This agrees well with the formulæ assigned to them, the former having the nitro-group in the ortho-position relatively to the hydroxyl, while in the latter case it is in the para-position.

Again, Guareschi's isomeride can be hydrolysed by warm fuming sulphuric acid, or by fusion with potash, whereas Holtzwart's isomeride cannot.

On reducing the two nitro-compounds, characteristic differences are obtained in the reactions of the amino-derivatives; while that from Guareschi's isomeride gives no colour with ferric chloride, and in alkaline solution has a strong blue fluorescence, the amino-derivative of Holtzwart's isomeride gives an indigo-colour with ferric chloride, and becomes cherry-red in presence of ammonia. These reactions are also given by Collie's acid after nitration and reduction, whence it follows that they have the same configuration.

The author failed to obtain, by the action of phosphorus pentachloride on his compound, the substance $C_8H_6N_2$, described by Holtzwart.

From the pseudolutidostyril obtained in these experiments, the following derivatives were obtained:—

(1). 3 : 5-*Dibromo-ψ-lutidostyril*, melting at 253° (corr.).
(2). 5-*Nitro-ψ-lutidostyril*, melting at 254° (corr.).
(3). 3-*Nitro-ψ-lutidostyril*, melting at 196° (corr.).

ANNIVERSARY MEETING, *March 28th*, 1901.

Professor THORPE, C.B., F.R.S., President, in the Chair.

DR. JOWETT and Mr. WERNER were appointed scrutators, and a ballot was opened for the election of Officers and Council for the ensuing year, the ballot being closed at the conclusion of the President's Address.

The PRESIDENT, in beginning his Address, said that the Chemical Society was founded about four years after the accession to the throne of the Gracious Lady whose recent loss they deplored, and the memory of whose virtues and worth as a woman and as a monarch would for ever abide with them. He was proud to think that this Society, in so far as it had ministered to the progress of chemistry, may have contributed in some measure to the lustre of a reign so pre-eminently associated with the development and spread of science in this country, and with the extension of those arts which rest upon chemistry. The Society was not unmindful of what the science owed to the Royal Family, and in particular to the late Prince Consort, whose appreciative interest in the fortunes of the Royal College of Chemistry, of which he was the President, and whose friendship for the eminent man who made it the first organised school of chemical research in this country, had directly ministered to its own activity, welfare, and usefulness. The Society had sought to give utterance to these sentiments in an Address which it ventured to submit to His Majesty on his accession to the Throne, and in respectfully tendering its congratulations, and in offering its homage, it expressed the hope that his reign would be marked by discoveries in the science it represented not less brilliant than those which characterised the reign of his illustrious mother.

The following Fellows have died:—Edmund Atkinson, John Borland, Alfred Hunter Boylan, Wm. Harcourt Branscombe, Sir John Conroy, Henry Howard Crawley, Thomas Flower Ellis, Frank W. Harris, Herbert A. Hotblack, Sir John Bennet Lawes, Stevenson Macadam, Frederick Alfred Manning, William McConnell, William Parsons, Richard Reynolds, Saville Shaw, George Smith, C. J. H. Warden, Augustus A. Wood, Thomas M. Wyatt.

The numerical strength of the Society was as follows:—

Number of Fellows, March 29th, 1900		2292
" " since elected		117
" " reinstated by Council		5
		2414
Removed on account of non-payment of two annual subscriptions	28	
Withdrawn	31	
Deaths	20	
	—	79
Number of Fellows, March 28th, 1901		2335
Foreign Members		33

The President offered on behalf of the Society its warm congratulations to its former President and Treasurer, Dr. Russell, on the attainment this year of his jubilee as a Fellow of the Society. Mr. Nevil Story Maskelyne, a former President of the Society; Sir David Gamble, C.B.; and Mr. Edward Riley were also congratulated on reaching this anniversary.

During the year, the Society had joined in the commemoration of the fortieth year of the doctorate of Professor Markownikoff of Moscow, one of its distinguished Foreign Members.

Since the last Anniversary, 182 communications had been made to the Society, a number greater than in any preceding year. In character, variety, and importance they compared not unfavourably with the contributions of any former period. Abstracts of all these had appeared in the *Proceedings*, while 106 have already been published in the *Transactions*. The volume of *Transactions* for 1900 contained 127 memoirs, occupying 1334 pages; in the preceding year 120 papers were published, occupying 1166 pages. The President drew particular attention to the desirability of brevity in the papers communicated to the Society.

The volumes for 1900 contains 3758 abstracts of papers, published mainly in continental journals, occupying 1492 pages, arranged as follows:—

	Pages.	No. of Abstracts.
PART I.		
Organic Chemistry	712	1355
PART II.		
General and Physical Chemistry		467
Inorganic Chemistry		383
Mineralogical Chemistry		174
Physiological Chemistry		336
Chemistry of Vegetable Physiology and Agriculture		368
Analytical Chemistry		675
	780	2403
Total in Parts I. and II. ..	1492	3758

The number of abstracts dealt with in 1900 is 141 more than in the preceding year, though occupying 304 pages less.

The volume for 1900 contained no less than four Memorial Lectures, giving an account of the life-work of Victor Meyer, Bunsen, Friedel, and Nilson. The Council had determined to issue those Memorial Lectures which had appeared up to the end of 1900 in a separate form. The President in this connection paid a special tribute to the late Prof. FitzGerald, who had delivered the Helmholtz Memorial Lecture, one of the most weighty of the series.

A special reference was made to the bearing of the Copyright Bill upon the Society as a publishing agency.

As regards the Library, 810 books had been borrowed, as against 790 last year; and 95 books, 327 volumes of periodicals, and 30 pamphlets had been added, as against 114 books, 397 volumes of periodicals, and 27 pamphlets in the preceding year.

A number of books and periodicals not bearing in any way on the work of the Society had been removed from the library. Some proportion of these had been offered to and accepted by the British Museum; the remainder will be disposed of either by presentation to kindred societies or otherwise. The need of shelf room was pressing in view of the fact that the present accommodation would be exhausted in two years. The Library Catalogue was within sight of completion; it included 6300 author entries and nearly as many subject entries. An estimate for printing was in preparation.

The President, referring to the result of the voting on the question of the day and hour of meeting, said the Committee had reported to the Council that the returns, however, analysed, showed such a large majority in favour of the proposed change, that the Council had decided that it should be provisionally tried during the coming session. The Ordinary Meetings of next session would therefore be held on the first and third Wednesdays of the month at 5.30 p.m.

A reference was made to the movement for a uniform system of atomic weights, and it was announced that the Atomic Weights Committee had decided to recommend—(1) That O = 16 be taken as the basis of calculation of atomic weights; (2) that in assigning a number as the atomic weight of any element only so many figures should be employed that the last may be regarded as accurately known to one unit in that figure.

Grants amounting to £160 had been made from the Research Fund in aid of chemical investigation.

Dr. Armstrong proposed a vote of thanks to the President, coupled with the request that he would allow his Address to be printed in the *Transactions*.

Prof. Smithells seconded the motion, which was carried by acclamation.

The President having returned thanks,

Prof. Tilden, F.R.S., the Treasurer, in giving an account of the balance sheet, which he laid before the Society, duly audited, said:—

The receipts had been:—By admission fees and subscriptions, £4290; by sale of Journal and advertisements, £880 12s. 9d.; and by dividends on invested capital, £464 14s. 4d. The total receipts from all sources amounted to £5668 19s. 8d. The expenses had been:—On account of the Journal, £3512 9s. 11d.; on account of the Proceedings, £250 15s.; on account of the preparation of a new Catalogue, £51 16s. 4d.; on account of the Library, £238 15s. 11d.; House expenses, £210 9s. 11d. The total expenditure being £4832 3s. 9d.

The Treasurer, in concluding, proposed a vote of thanks to the auditors, which was acknowledged by Mr. Page.

Prof. Emerson Reynolds, F.R.S., proposed a vote of thanks to the Officers and Council.

Prof. Collie, F.R.S., seconded the motion, which was unanimously adopted.

Prof. Dunstan, F.R.S., responded.

The scrutators having presented their report to the President, he declared that the following had been duly elected:—

President—J. Emerson Reynolds, D.Sc., M.D., F.R.S.

Vice-Presidents who have filled the office of President—Sir F. A. Abel, Bart., G.C.V.O., K.C.B., D.C.L., F.R.S.; H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir W. Crookes, F.R.S.; James Dewar, M.A., LL.D., F.R.S.; Sir J. H. Gilbert, Ph.D., LL.D., F.R.S.; J. H. Gladstone, Ph.D., D.Sc., F.R.S.; A. Vernon Harcourt, M.A., D.C.L., F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, LL.D., Ph.D., F.R.S.; Sir H. E. Roscoe, D.C.L., LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; T. E. Thorpe, C.B., Ph.D., D.Sc., LL.D., For.Sec.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents—E. Divers, M.D., D.Sc., F.R.S.; C. E. Groves, F.R.S.; Prof. Herbert McLeod, F.R.S.; Prof. H. A. Miers, M.A., F.R.S.; T. Purdie, Ph.D., F.R.S.; T. Stevenson, M.D.

Secretaries—Wyndham R. Dunstan, M.A., F.R.S.; A. Scott, M.A., D.Sc., F.R.S.

Foreign Secretary—Raphael Meldola, F.R.S.

Treasurer—William A. Tilden, D.Sc., F.R.S.

Other Members of Council—H. Brereton Baker, M.A.; F. D. Chattaway, Ph.D., D.Sc.; Frank Clowes, D.Sc.; A. W. Crossley, Ph.D., D.Sc.; A. E. Dixon, M.D.; Prof. J. J. Dobbie, M.A., D.Sc.; H. J. H. Fenton, M.A., F.R.S.; M. O. Forster, Ph.D., D.Sc.; D. Howard; S. U. Pickering, M.A., F.R.S.; W. J. Pope; James Walker, D.Sc.

Anniversary Dinner.

The Anniversary Dinner of the Society took place at the Whitehall Rooms, on Wednesday, March 27th, at 7 p.m.

In proposing the loyal toasts, The President, while paying the Society's tribute to the late Queen, said they could have no manner of doubt that the King would worthily follow in her footsteps. That the King would long rule over the splendid heritage to which he had succeeded, and that his reign might be marked with the same full measure of prosperity, intellectually and morally which had graced the reign of Victoria, was their constant hope and confident anticipation.

The Treasurer, Professor Tilden, in proposing the toast of the Houses of Legislature, said they did not seek the honour of the presence of so many members of both Houses at their Dinner that evening solely for the purpose of enjoying their society. The fact was the Chemical Society, old and respectable as it was, had to give a sort of account of itself in the face of the world, and nowhere was it so important that the objects of the Society, and the benefits they thought it conferred upon the community, should be recognised as in the Houses of Legislature. Some of them were rather anxious as to the part which science had to play and the position which science was to occupy in the national programme. Science demanded a much more influential place in the councils of the nation than had hitherto been granted it.

The Lord Chancellor, in responding for the House of Lords, said he had feared from the Treasurer's speech that they were about to be subjected to a quantitative and qualitative analysis, but was glad to see it pass off into a homily upon the importance of infusing into Parliament a more scientific spirit. He was always glad to use the phrase Parliament, because although, for obvious purposes, it was desirable that it should be divided into two Chambers, he always liked to regard that great instrument of human enlightenment and freedom as being one, and he would lament anything which interfered with the working of that great constitutional machine. He believed that the House of Commons had that day been distinguishing itself in its energy to procure chemically pure beer. (Laughter). He, unfortunately, had no such claim to make for the House for which for the moment he had the honour to respond. He did not believe they had been dealing either with beer or science during this Session, except so far as military science might be supposed to demand public attention. He accepted with the most perfect good faith the exhortation which he had received from the proposer of the toast, and so far as he could influence either public opinion or the action of the House of Lords, he would never forget what they owed to science. He had heard it whispered—he would not say by unkind friends—that their work in manufacturing Acts of Parliament was not absolutely perfect, but the more they advanced in the science of language, in perfecting precision in organising human thought and reasoning, the plainer they would make to the popular understanding the meaning of an Act of Parliament. Nothing could more induce to the making of clear laws than a scientific education, which would bring about an assiduity of reasoning and clearness of thought.

Sir Herbert Maxwell, Bart., M.P., in responding for the House of Commons, said though much had been said in condemnation of that House he submitted that its present Members were not worse than those who had gone before. Though they might conduct their business in a way which would disgrace a self-respecting company, they were not so indifferent to the work of scientists as they appear to be. They would, for instance, as soon condemn a witch to be burnt as discuss a subject of a scientific nature, such as that which had occupied them that afternoon, without taking the advice of the experts of the question. He asked that they would rather judge of the result of their labours than the way in which that result was attained. He took the opportunity of specially thanking the Chemical Society for the aid and hospitality it had recently afforded the Committee on Food Preservatives, of which he was Chairman.

Lord Kelvin, in proposing the toast of The Chemical Society, said he was perfectly appalled at the magnitude of the work he was asked to commend to their notice. When he thought of all that had been done in chemistry during the last century, he was convinced he would in no way be exaggerating when he said that chemistry was the first and last science of the nineteenth century. It only began to exist as a science at the close of the eighteenth century. He was a physicist, and he could assure them that physicists had to go to chemistry all through their work. The physicist wanted to measure everything, and now in particular they wanted to know the weight of an atom of hydrogen and the number of molecules in a litre of hydrogen. They were, he was glad to say, in a fair way of learning it, thanks to the labours of chemists. Chemists must stick to dynamics. The chemist had to do with the forces between particles of matter from the hundred-millionth of a grm. in weight to the thousand-millionth, and had to look to the forces between them, and tell the number of their particles in a litre of water or beer, and say how many of those atoms were arsenic, and how many atoms of arsenic might be allowed. They had learned within the month that some amount of arsenic might be allowed—that without arsenic man could not exist, that an essential in the composition of the human body was the seventeen-hundredth of a grm. of arsenic in the thyroid gland. Chemistry was the first and the last science of the nineteenth century, and only recently had given them what ancient chemists would have been glad to have seen—namely, liquid air and liquid hydrogen. He referred eloquently to the work of the great chemists of the past, especially of the first President of the Society, Professor Graham, and to that of Lord Rayleigh and Professors Ramsay and Dewar. To their labours the physicist owed much, and there was no reason whatever why chemistry and physics should not go hand in hand, helping one another, and working cordially together for the advancement of knowledge. Some of the work of the physicist was looked upon as drudgery. Chemists knew a great deal about drudgery, too, and did not shrink from it. Lord Rayleigh devoted himself to working painfully and laboriously at an object which looked trivial, the finding of the density of atmospheric nitrogen, and he discovered that it contained a gas that had never even been suspected before. That was a triumph for drudgery. In looking back to the early history of the Chemical Society he took some pride in thinking that Glasgow took its part, in that it provided the first President, and that Dr. Thorpe had been Professor of Chemistry at the Andersonian Institute there. The Chemical Society though but young, only 61 years old, had a glorious past, and he believed a splendid and prosperous future before it.

The President, in reply, said no matter how they regarded the Society, whether from the point of view of its numerical strength or from the character of its scientific output, or from the lower ground of its financial condition, he thought there was no constitutional infirmity about it. This happy result was largely to be attributed to that constant accession of strength they gained in the increase of membership. There was no English chemist of note who was not proud of being a member of their body, whilst they had in their ranks almost every foreign chemist of prominence. The honorary membership of their Society was a distinction as highly prized as any mark of recognition which a body of scientific workers could bestow. There were signs of many changes in the chemical world, but whatever the future might have in store for them, he who occupied the presidential chair in the 2001, and who in ushering in the new century sought to know what was being done when the preceding century was dying, would, he was convinced, do them the justice to recognise that they who collectively made up that body corporate were, according to their several rights and within the measure of their individual powers, doing what within them lay to further the true object of their calling as men of science, the attainment of the truth for the sake of the truth.

Professor Dewar, in proposing the toast of the Learned and Scientific Societies, said that whenever any body of men had associated themselves for the purpose of discovery, invention, or the verification of truth, then the Chemical Society was most desirous of recognising the advantage of their labours on behalf of the community and of chemistry especially. Chemists were particularly desirous of recognising the great benefits which accrued from the corporate action of so many minds in the multitudinous departments of scientific work. He spoke of the dangers of exaggerating the importance of personality in matters of scientific research, as scientific work was always based on the labours of the past.

Mr. A B. Kempe, Treasurer of the Royal Society, in reply, said there was one point on which the progress of their Society was not so satisfactory as he could wish it to be. That was in the matter of financial support. It was true they had much to thank private beneficence for, and he thought it was a matter of congratulation that His Majesty's Government had in the person of Mr. Balfour recognised the value of pure science. As Treasurer of a scientific society, however, he felt, and he was sure treasurers of other societies felt the same, that they might promote the interests of mankind rather more than they did at present, if they had a little more money to devote to the work.

Professor S. P. Thompson, F.R.S., referred particularly to the great work chemists had done in the matter of artificial illumination. He trusted the century now opening would see still greater advances, and that the scientific bodies wherever their work seemed to cross or coincide would work hand in hand for the good of all.

Professor Emerson Reynolds, President-Elect, proposed the toast of the Guests, which was responded to by Sir W. S. Church and Sir Francis Mowatt.

Sir Henry Roscoe proposed the health of the Chairman.

NOTICES OF BOOKS.

A Manual of Laboratory Physics. By H. M. Tory and F. H. Pitcher. New York: John Wiley and Sons. London; Chapman and Hall, Ltd. 1901. Pp. x.—288. 8vo., Ill.

The authors of this Manual have embodied in its pages their experience in teaching large classes at McGill University, Montreal; the course comprises experimental studies in Sound, Light, Heat, Magnetism, and Electricity. The method of presentation is distinctly practical; each exercise begins with a list of references to standard text-books of physics, a list of the apparatus required, and then follows the theory of experiment, practical directions, and lastly an example of the method of reporting results, which includes a blank to be filled in by students. The mathematical knowledge required to follow the course is only moderate, the calculus is not used; diagrams illus-

trate the experiments wherever necessary; in short, the book is well arranged and carefully adapted to its purpose. The proof reading seems to be accurate, but on p. 40, for RO read PO. There is an index. H.C.B.

CORRESPONDENCE.

AMERICAN *v.* ENGLISH SPELLING.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS of March 22nd (vol. lxxxiii., p. 141), there appeared a letter from Dr. H. Carrington Bolton, of Washington, in regard to the American spelling of chemical words, defending the use of such forms as *oxid, sulfur*, &c. I am not an American citizen myself, but have lived in the United States the larger part of my life, and hence may be allowed to remark that the statement of Dr. Bolton, "the American authors use a definite system, endorsed by high authorities in the United States," is rather an *over*-statement. The rules for the spelling and pronunciation of chemical terms which are referred to as prepared by a Committee of the Chemical Section of the American Association for the Advancement of Science were adopted by a very small number of the chemists of the United States at a meeting in Washington in 1891, and are acted upon by but a small number of "reformers."

It is proverbially useless to dispute about matters of taste, and I have never taken any part in argument with those whose taste leads them to print a scientific book on paper so that it looks like a bad specimen of the so-called "dialect story"; but as regards the single reason given by Dr. Bolton in his letter for a change of English spelling in the case of the word sulphur, I am inclined to think that his philological argument is not sound. He says, "I wish to point out that the word 'sulphur,' spelled as if derived from Greek, is etymologically incorrect, and is being replaced by 'sulfur' on this side of the Atlantic." The word in question is found in Latin works in the three forms—sulfur, sulphur, and sulpur; and of these the last named is, I believe, the most ancient—it appears in the oldest manuscripts of Lucretius. It is easy to see how "sulpur" may have received an "h," originally as a mere aspirate of the second vowel, and after the "p" and "h" had acquired the blended sound like that of, though not derived from, the Greek ϕ. This sound came in later times to be represented by "f," but the reverse order of change seems inadmissible. Not being entitled to write as an expert on this point I should be glad to see it discussed by good classical scholars.—I am, &c.,

J. W. MALLET.

University of Virginia, U.S.A.,
April 6, 1901.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxii., No. 13, April 1, 1901.

Some Osmyloxalates.—L. Wintrebert.—During a previous research, the author determined the constitution of potassium osmyloxalate, $OsO_2(C_2O_4)K_2.2H_2O$, and proved the existence of corresponding silver and sodium salts. Since then, he has determined the conditions under which the two latter bodies can be easily obtained, and also prepared certain other osmyloxalates:—Sodium osmyloxalate, $OsO_2(C_2O_4)_2Na_2.2H_2O$; ammonium osmyloxalate, $OsO_2(C_2O_4)_2(NH_4)_2.2H_2O$; silver osmyloxalate, $OsO_2(C_2O_4)_2Ag_2$; barium osmyloxalate, $OsO_2(C_2O_4)_2Ba.4H_2O$; abnormal barium osmyloxalate, $OsO_2(C_2O_4)_3Ba_2.6H_2O$; strontium osmyloxalate, $OsO_2(C_2O_4)_2Sr.4H_2O$; and calcium osmyloxalate, $OsO_2(C_2O_4)_2Ca.2H_2O$.

Reducing Properties of Magnesium and Aluminium.—A. Dubois.—Magnesium and aluminium reduce nearly all oxides; evidently those in which the metal, when combining with oxygen, evolves more heat than hydrogen when it combines with oxygen to form water. It is apparent, then, that these two metals ought to act energetically on water. The author shows this to be the case by two brilliant experiments. He finds that if 4 atoms of aluminium are mixed with a molecule of alumina and a light applied, they react with great vigour, giving the oxide Al_2O. He also effects a number of reductions in hydrogen.

Cinchonine.—E. Jungfleisch and E. Léger.—In this research, the authors endeavour to find the proportion of cinchonine in hydrocinchonine, to show that the properties attributed to cinchonine correspond in reality to a mixture, and, indeed, to find what are the properties of pure cinchonine.

Some Iodo-derivatives of Phenol.—P. Brenans.—In a previous research, the author examined the action of a solution of iodine in iodide of potassium on phenol in alkaline solution. He now investigates certain unexpected results obtained by means of the same reagents, but under different experimental conditions. He obtains, under the conditions adopted, di-iodophenol, $OH—C_6H_3—I_2.1.2.4$, accompanied by tri-iodophenol, $OH—C_6H_2—I_3.1.2.4.6$, and, under slightly varying conditions, the tri-iodophenol alone.

Action of the Ethers of Bibasic Acids on the Organo-metallic Compounds.—Amand Valeur.—The action of the organo-metallic derivatives of zinc or magnesium on an ether-salt results in the transformation of the group $R—CO_2C_2H_5$ into $R—C\begin{matrix}R'\\R'\end{matrix}OH$. With the ether derivatives of the bibasic acids the author obtains twice this reaction, and so arrives at the bi-tertiary glycols.

The Organo-metallic Compounds of Magnesium.—MM. Tissier and Grignard.—It has already been shown that magnesium reacts with great facility on the halogen derivatives of the alcohols when in ether solution, giving the compound $C_nH_{2n+1}—Mg—(M')$; where M' denotes an atom of Cl, Br, I, which is capable, in the same manner as zinc methyl, of reacting on various organic compounds. At the same time a secondary reaction takes place which gives rise to saturated carbides by the splitting off of two monovalent groups, C_nH_{2n+1} and formation of $Mg(M')_2$: $2[C_nH_{2n+1}(M')] + Mg = Mg(M')_2 + C_nH_{2n+1}—C_nH_{2n+1}$. Magnesium behaves in this case in an analogous fashion to the alkaline metals. The influence of this secondary reaction increases with the accumulation of the carbon atoms in the molecule of the halogen derivative, being less noticeable in the lower terms of the series, and ending by being equal to the principal reaction in terms of C_6.

New Reactions of Organo-magnesium Compounds.—Ch. Moureu.—The action of magnesium ethyl iodide on amyl nitrite and on nitromethane forms, in both cases, diethylhydroxylamine. These two reactions may be generalised. These precise facts, and certain experiments which the author mentions, establish clearly that the oxygen compounds of nitrogen and of sulphur react on organo-magnesium derivatives. Doubtless the acid-oxygen compounds of other elements react in a similar manner, and the author intends to further investigate this matter.

Ethero-organo-magnesium Derivatives.—E. E. Blaise.—The author's experiments show that when an alcoholic halogen derivative reacts on magnesium in pre-

sence of anhydrous ether, an ether derivative is obtained, of remarkable stability and possessing the composition $RMgX(C_2H_5)_2O$. Under these conditions, ether is not a mere solvent, it enters into the reaction itself, and the stability of the product obtained shows that it is intimately united to the rest of the molecule. If ether is replaced by another solvent, the other conditions of the experiment being identical, the reaction does not take place.

New Synthesis of Aniline.—George F. Jaubert.—The author effects the synthesis of the aromatic amines according to the equation $C_6H_6+NH_2.OH=C_6H_5NH_2+H_2O$. He uses zinc chloride, sulphuric anhydride, and aluminium chloride to effect condensation.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxiii., No. 24.

Estimation of Oxygen in Commercial Copper.—Maurice Lucas.—Oxygen is generally estimated in copper by two methods, viz., reduction by hydrogen and measuring the loss of weight, which represents the oxygen and the volatile metals; or by treatment with nitrate of silver and estimation of the copper in the residue. The author has devised a third method, which consists of melting the copper with tin in the electric furnace in a current of carbonic oxide; the carbonic acid formed is then collected and weighed. The copper and the quantity of pure tin necessary to form a 20 per cent alloy are placed in a tared porcelain boat in the cool part of a porcelain tube, and the carbonic oxide gas passed over it for a quarter of an hour; then fix on the potash and sulphuric bulbs, previously weighed full of air. The porcelain tube is then gradually moved until the boat is in the hot part; the temperature is maintained at 900° for an hour. The bulbs are then disconnected and weighed again full of air. The boat is allowed to cool by moving the porcelain tube back to its original position, and the boat is weighed. In this manner we get—(1) The weight of CO_2 formed, which multiplied by 0·364 gives the oxygen set free; (2) the loss of weight, which represents the oxygen and the volatile bodies (As, Sb, &c.). This method has been tried with pure suboxide of copper and with known mixtures of Cu_2O+Sn, $Cu_2O+Sn+Cu$, &c., and the effect of impurities was determined by the addition of salts, such as arseniate, phosphate, &c., of copper, to the boat containing the pure copper and tin. This method can be generalised and applied to all metals whose oxides are reduced by carbonic oxide.

The Composition of a Calcic Sulphate Water from Lautaret (Hautes-Alpes).—J. A. Muller.—The temperature of the principal spring, taken repeatedly during the months of August, September, and October, averaged 25·3°, the greatest variations being 25·0° and 25·5°; its flow is about 2000 litres per hour. The complete analysis of this water has given the following results:—

	Weight per kilogrm. Grms.
Carbonate of calcium	0·893
Sulphate of calcium	0·715
Tricalcic phosphate	0·002
Sulphate of magnesium	0·667
Sulphate of sodium	1·429
Sulphate of potassium	0·083
Chloride of sodium	1·379
Silica	0·044
Ferric oxide	0·004
Total	5·216
Residue at 180°	5·167

There was also a slight trace of fluorine met with. The deposit formed round the mouth of the spring was also analysed, and gave the following results:—

Moisture at 115°	0·83
Insoluble in dilute nitric acid (dried at 115°)	0·22
Silica	0·46
Oxide of copper	0·03
Ferric oxide	1·60
Carbonate of lime	91·12
Sulphate of lime	2·95
Phosphate of lime	0·31
Fluoride of lime	Traces
Carbonate of magnesium	0·65
Sulphate of sodium	1·30
Chloride of sodium	0·09
	99·56

The αβ-Dimethylglutolactonic Acids.—E. E. Blaise.—Already noticed.

The Evolution of Terpenic Compounds in the Geranium.—E. Charabot.—Already noticed.

Acetals of Monovalent Alcohols; Thermo-chemistry.—Marcel Delépine.—Already noticed.

Acetals of Plurivalent Alcohols.—Marcel Delépine.—Already noticed.

The Estimation of Arsenic, and its Determination in the form of Ammonio-magnesian Arseniate.—O. Ducru.—Already noticed.

MISCELLANEOUS.

City and Guilds of London Institute.—His Majesty the King has graciously consented to become Patron of the City and Guilds of London Institute, of which as Prince of Wales he has been President since 1881.

New Method for obtaining Non-saturated Hydrocarbides.—L. A. Tchougaef.—This process is founded on the decomposition undergone by some xanthogenic compounds by dry distillation; this decomposition has been in the first place thoroughly examined for the particular case of the transformation of menthol into menthene. Mentholate of soda, by fixing the elements of CS_2, gives menthylxanthogenate of soda, which, when warmed with iodide of methyl in ethereal solution, gives crystallised methylic ether, $C_{10}H_{19}O—CS—SCH_3$, fusible at 38—39°, boiling at 153° under 15 m.m. pressure, with decided decomposition. It is insoluble in water, but soluble in ether, benzene, and chloroform. When heated to over 160° this substance melts and decomposes according to the following formula:—

$$C_{10}H_{19}O—CS—SCH_3=C_{10}H_{18}+CH_3—HS+CSO.$$

In a well-cooled recipient, menthane and methylic mercaptan condense. By evaporation of the volatile products and repeated distillation over sodium we obtain menthene, boiling at 167—168°; the return is 70 per cent of theory. Menthene thus obtained has very definite properties, $d_0^0=0·8132$; $[\alpha]_D=+114·77°$ to 116·06° (such a high rotatory power has not yet been observed for menthene). The author is of the opinion that this method of preparing menthene is the only one up to the present time which does not give rise to isomerisations. Identical results are to be obtained with other menthylxanthogenic ethers (ethylic, benzylic), and also with dimenthyldixanthogenic ether, $C_{10}H_{19}O—CS—S—S—CS—OC_{10}H_{19}$. This latter is obtained by the action of iodine on menthylxanthogenate of soda, and occurs in beautiful crystals, fusible at 90—91°. By dry distillation it decomposes principally according to the following equation:—

$$C_{10}H_{19}O—CS_2—S_2C—OC_{10}H_{19}=$$
$$=C_{10}H_{18}+C_{10}H_{19}OH+S+CS_2+COS.$$

By fractionation of this product over sodium we obtain

menthene, boiling at 167—168°, $[\alpha]_D = +90{\cdot}97°$. The author has prepared, by this method and using borneol, a crystallised camphene, and with octylic alcohol a caprylene boiling at 122—123°. He is now engaged in the study of how far the method can be generalised. According to his results the superiority of this process is due to the facility with which the xanthogenic compounds are decomposed, and to the fact that the reaction takes place without the intervention of any energetic reagents, such as acids, capable of producing isomerisation.—*Journ. Soc. Phys. Chim. R.*, vol. xxxi., p. 959.

MEETINGS FOR THE WEEK.

MONDAY, 29th.—Society of Arts, 8. (Cantor Lectures). "Alloys," by Sir William Chandler Roberts-Austen, K.C.B., F.R.S.

TUESDAY, 30th.—Royal Institution, 3. "On Cellular Physiology, with special reference to Enzymes and Ferments," by Allan Macfadyen, M.D., B.Sc.

—— Society of Arts, 4.30. "The British West Indies," by Sir Nevile Lubbock, K.C.M.G.

WEDNESDAY, May 1st.—Society of Public Analysts, 8. "Alkaline Waters from the Chalk," by W. W. Fisher, M.A., F.I.C. "Citron Oil," by Herbert E. Burgess. "Arsenic in Coal and Coke," by Alfred C. Chapman, F.I.C.

—— Society of Arts, 8. "Thames Steamboat Service," by Arnold F. Hills.

—— Royal Institution, 5. (Annual General Meeting).

THURSDAY, 2nd—Chemical, 8. Ballot for the election of Fellows. "The Synthetical formation of Bridged-rings—Part I., Some Derivatives of Bicyclopentane," by W. H. Perkin, jun., F.R.S., and Dr. J. F. Thorpe

—— Royal Institution, 3. "Arthur Sullivan" (with Vocal and Instrumental Illustrations), by Sir Alex. Campbell Mackenzie, Mus.Doc.

FRIDAY, 3rd.—Royal Institution, 9. "Memory," by Charles Mercier, M.B., F.R.C.S., M.R.C.P.

—— Society of Arts, 8. (Howard Lectures). "Polyphase Electric Working," by Alfred C. Eborall, M.I.E.E.

SATURDAY, 4th.—Royal Institution, 3. "Climate, its Causes and its Effects," by John Young Buchanan, M.A., F.R.S.

TO CORRESPONDENTS.

Rev. E. Rattenbury Hodges.—The spectroscope shows nothing but lime.

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THE CHEMICAL NEWS.

Vol. LXXXIII., No. 2162.

VITRIFIED QUARTZ.*

By W. A. SHENSTONE, F.R.S.

In spite of the great improvements introduced into the art of glass making by Abbe and Schott, which have led to marked advances in microscopy, in thermometry, and in other directions during the last quarter of a century, glass is still unsuitable for many of the purposes to which we put it, and there remains a real need for some plastic material, more infusible, more insoluble, more fully transparent, more elastic, and more stable under changes of temperature than glass.

Such a substance exists in the form of vitrified quartz, or vitrified silica as I shall prefer to call it.

Vitrified silica was first made in 1839 (*Comptes Rendus*, viii., 678, 711), by M. Gaudin, who spun threads of it by hand and noticed their flexibility; made small, very hard pellets of it by dropping fused quartz into cold water, and observed that in this form it was inactive to polarised light.† It was re-discovered in 1869 by M. Gautier (*Comptes Rendus*, cxxx., 816), who made capillary tubes and spirals of vitreous silica, and exhibited them at the Paris Exhibition in 1878; but who failed to obtain larger objects even with the aid of the electric furnace. Finally, it was yet once again independently discovered, in 1889, by Professor C. V. Boys, who used the torsion of "quartz fibres" for measuring small forces, and produced fine tubes and small bulbs of the same material; and who was the first to really recognise the great value of this remarkable substance.

As all who are here to-night are not chemists, I may remind you that quartz, or rock crystal, has for some time past been used by spectacle makers, and in the construction of optical instruments; and that it is a form of oxide of silicon,‡ which is very familiar to us all in the forms of sand and flint. Quartz is occasionally found in magnificent masses, but our chief source of supply is Brazil, where it occurs in large fragments like those on the table.

Quartz itself exhibits many of the desirable qualities enumerated above. It is hard, transparent to the ultra-violet rays, difficult to melt, a good insulator, and insoluble in most solvents, but it bears sudden changes of temperature very badly, and therefore it is very difficult to manipulate quartz at high temperatures. When it has been vitrified by heat, however, it becomes much more tractable, and in the vitrified state (vitrified silica) it is not very difficult to deal with.

It is about this "vitrified silica," how to prepare it and fashion it into apparatus when plastic, and about its properties and uses, that I am about to address you to-night.

The first obstacle met by those who wish to obtain vitrified silica is caused by the tendency of quartz to splinter. It will not bear contact with a flame. As you see, when a piece of quartz is thrust into a flame it cracks and falls to pieces, and the fragments again break up when similarly treated. Consequently it was very difficult for the pioneer workers to soften it in the flame. It is true that if the quartz be broken small and heated to redness in a crucible it becomes more easy to manage; but even then it gives trouble, and I should not like to say how much my first silica tube, which held about 5 c.c., had cost for oxygen and labour when it was finished.

Fortunately we have found that we can overcome the splintering of quartz by heating it in small fragments to about 1000° C., and throwing it quickly into cold water. As you see, it then becomes white and enamel like, and after the treatment has been repeated the product, though still in masses, may be thrust suddenly into the hottest part of an oxy-hydrogen flame without splintering to the slightest extent. The preparation of this non-splintering silica constitutes the first stage of the process we are about to show you.

Another difficulty is connected with the oxy-gas burner. Vitrified silica only becomes sufficiently plastic for our purpose when it is above the melting-point of platinum; and it cannot be heated sufficiently in all parts of an oxy-gas flame. What is wanted is not so much a very large flame as one which presents a very hot spot (this is situated just beyond the inner blue cone of the flame). After trying all sorts of burners, I have concluded that the "mixed gas" jets give the best results, and the injector burner of Mr. Jackson, of Manchester, is decidedly the best I have met with.

The first step in the process of converting the white enamel-like non-splintering silica into tubes and other vessels consists in pressing together the heated ends of two small fragments of it, held in platinum forceps, till they adhere, and adding a third lump, then a fourth, and so on, until a rough rod has been made. This rod is afterwards re-heated, and drawn out into finer rods, about 1 m.m. in diameter; care being taken to heat each fresh mass of material slowly, and from below upward in order that there may be as few bubbles as possible in the product.

A few of the fine rods of silica are bound round a stout platinum wire, or twisted into a spiral whilst soft (Boys and Dufour's method), and heated in the flame till their sides adhere. The uncouth tube thus produced is re-heated, drawn out, and closed at one end. A bulb is blown on the closed end in the usual manner, and this, when again drawn out, gives us a fine and fairly regular tube, which can be lengthened by adding silica to one end of it, blowing a new bulb from this, and drawing it out as before.

The enlargement of the small bulbs was rather difficult at first. My earliest attempts consisted in adding small lumps of silica to one end of a bulb, softening them in the flame, and expanding the bulb by blowing. It is not impossible to succeed in this way, though the vessels so produced are apt to be uncouth in appearance. But the process is unsatisfactory owing to the fact that often the thinner parts of the bulb immediately surrounding the mass to be expanded become hotter and softer than the latter. When this happens the bulb bursts, and as it can only be repaired by the addition of fresh lumps of silica the process is apt to be tedious and expensive. After many failures, it occurred to me that I might develop the bulbs by applying thin rings of silica as shown in Fig. 1,

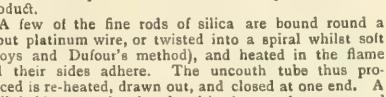


Fig. 1.

heating them until the silica begins to spread, and then expanding them by blowing. This method gave satisfactory results at once. By it we can produce long tubes, and other apparatus like those exhibited to-night, if not at a very quick rate or very low cost, yet with certainty and very much more quickly than before.

When a silica tube has been made it can be worked in the flame as easily, though not as inexpensively, as glass. Such a tube can be thickened readily by adding fresh rings of silica; it can be drawn out to various degrees of fineness and sealed hermetically, whilst all kinds of joints can be made easily. In one respect silica is easier to work than glass. It never breaks when thrust suddenly into the flame and finished apparatus needs no annealing,

* A Discourse delivered before the Members of the Royal Institution, Friday, March 8, 1901.

† A more recent observation made by Professor S. P. Thompson confirms this.

‡ Silicon was discovered by Berzelius in 1823.

One precaution must be taken. The eyes must be protected by black spectacles. The glass of which these are made must be very dark; so dark that white-hot silica does not look very bright when viewed through it.

I have spoken of silica as being easy to work. I do not mean you to understand, however, that it is easy to do what you see Mr. Lacell doing to-night. It is not easy to perform any operation of this sort with his wonderful precision, and especially it is not easy to work under the conditions enforced upon him now; for he can see nothing of the effects he produces, and must adapt his manipulations to my remarks, although he can hear the latter only very imperfectly.

The Properties and Applications of Silica.

Vitrified quartz is harder than felspar, but less hard than chalcedony. When cut with a file it breaks like glass. Its conducting power for heat is about equal to that of glass. Mr. Boys has shown that even in an atmosphere saturated with moisture it is a very good insulator. Its density (2·21)* is decidedly less than that of quarts (2·66), and almost identical with that of amorphous silica. Its optical properties have not yet been fully studied, but its approximate index of refraction has been determined by Professor S. P. Thompson by means of a small prism cut for the purpose by Mr. Hilger. It is decidedly less than that of quartz.

The melting-point of silica is not known, and it is plastic over a considerable range of temperature. When a platinum wire embedded in a thick tube of silica is heated from outside by means of an oxy-gas flame the platinum melts, and runs at a temperature at which the silica retains its shape.

Its rate of expansion has been studied first by H. Le Chatelier (*Comptes Rendus*, cxxx., 1703), and more recently by Professor Callendar. The former finds its mean coefficient of expansion between 0° and 1000° to be 0·0000007, but from the manner in which his material was prepared I think it probable that it was not quite pure. Professor Callendar has, within the last few days, examined the behaviour of a rod of pure vitrified silica prepared by my method. He finds its mean coefficient of expansion to be only 0·00000059, which is only 1/17 as great as that of platinum, and much smaller than that of any similar substance that has hitherto been studied. He finds also that the expansion of vitrified silica is exceedingly regular up to 1000°, and that if not heated above 1000° the rod returns very exactly to its original length when cold. Beyond 1000° he found a slight permanent elongation, although the rod was under compression. Professor Callendar was able to carry his experiments up to 1500°, which is very satisfactory, for it shows that vitrified silica remains solid, or practically solid, at this very high temperature. This is an important observation, as less carefully conducted experiments made by others had led me to fear that it became slightly plastic even at as low a temperature as 1000°. Above 1000° the rate of expansion diminishes rapidly, changing to a contraction at about 1200°.† On cooling from 1500° to 1200° it expands.

Fine rods of silica, and also quartz fibres, are apt to become rather brittle after being heated to redness. But we have not at present detected this defect in the case of thick tubes or rod.

The transparency of vitrified silica to ultra-violet rays has been carefully examined by Dr. A. Wynter Blyth, to whom I am greatly indebted.

A good illustration of his experiments is to be found in the results obtained by photographing the spectrum of the light produced by electric discharge between electrodes of an alloy of zinc, tin, cadmium, and mercury, using quartz prisms and lenses. When the light was made to pass through a plate of vitrified silica 3 m.m. thick, it was quite possible to photograph bands up to the cadmium line λ 2264, while the interposition of a similar plate of soda-glass completely cut off all radiations beyond the mercury line at λ 3125, and a plate of flint-glass was found to be still more opaque.

The advantage of quartz over glass for the spectroscopic examination of the light given out by gases in vacuum tubes is apparent from a consideration of this result.

The most remarkable property of vitreous silica is its behaviour under sudden changes of temperature. We have seen already that tubes of it may be plunged suddenly into an oxy-gas flame without injury, and I have mentioned the fact that apparatus made of silica needs no annealing. But this is not all; we may drop water on a rod of white-hot vitrified silica, or plunge a white-hot silica tube into cold water, or even, by Professor Dewar's kind aid, into liquid air, without injuring it in any way whatever; indeed, experiments seem to show that the material gains very distinctly in regard to its elasticity when it is thus treated. I need hardly point out how convenient tubes of such a material will be to chemists, or how many spoilt lecture experiments may be avoided in future by those who possess a silica tube.

This last property of silica and the splintering of quartz find an explanation in the results obtained by H. Le Chatelier (*Comptes Rendus*, cxxx., 1703), and by Callendar. These, as already explained (Fig. 2), show that its rate of expansion is exceedingly low, and, moreover, that at temperatures much above 1000° it contracts when heated. Under these circumstances it follows first that the strains set up in silica when it is suddenly heated or cooled are comparatively small in amount; and, secondly, that if, for example, vitrified silica be suddenly cooled, say from 1500° to temperatures below 1000°, the strains set up at the earlier stages of the cooling process will tend to neutralise those produced subsequently. These facts enabled Le Chatelier to predict the indifference of vitrified silica to sudden change of temperature (*loc. cit.*). But the phenomena had been observed previously and exhibited in this country.

The behaviour of quartz under changes of temperature is also very peculiar. This was studied by Le Chatelier in 1889 (*Comptes Rendus*, cviii., 1046). From his curves, which are given in Fig. 2, it may be seen that this form

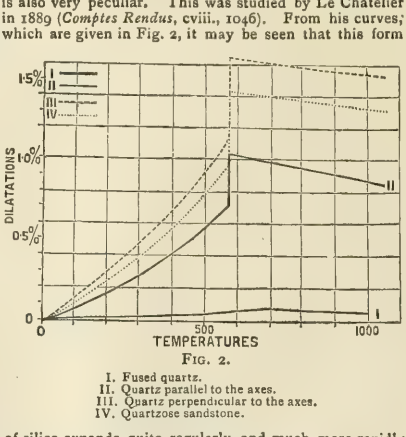


Fig. 2.

I. Fused quartz.
II. Quartz parallel to the axes.
III. Quartz perpendicular to the axes.
IV. Quartzose sandstone.

of silica expands quite regularly, and much more rapidly than vitreous silica up to 570°, but that at this temperature a sudden expansion takes place which is followed by a steady contraction on further heating.

One of the most important fields in which vitrified silica is likely to be useful is that of thermometry.

* This was determined by my pupil, Mr. T. Pears; the silica used contained a few minute bubbles.

† H. Le Chatelier's curve (Fig. 2), shows a similar contraction, but commencing at a somewhat lower temperature.

Owing to the small coefficient of expansion of vitrified silica, the degrees of silica-mercury thermometers will be of greater length in proportion to the volumes of their bulbs than those of mercury-glass instruments. Owing to its high melting-point it should be possible to employ it with advantage for measuring high temperatures by replacing the mercury by tin or other metal as has been done already by M. Dufour (*Comptes Rendus*, cxxx., 775). And whilst the great elasticity of vitrified silica suggests that the zero points of silica-mercury thermometers will be much more stable than those of glass instruments, the impunity with which it may be suddenly cooled from high temperatures promises obvious advantages.

Finally, the high melting-point of silica should make it very valuable for use in platinum thermometers, and I exhibit such a thermometer to-night which has been fitted up for me by Professor R. T. Glazebrook. As the applications of vitreous silica in thermometry are still under investigation I will not dwell on this part of the subject, except to add that, as glass reservoirs for air thermometers have proved disappointing, I am not without hopes that the new material may prove helpful in that department also.

We have not yet had time to examine the behaviour of silica with solvents, but if it acts like other forms of the same compound it may be expected to replace platinum for some purposes, as, for example, for condensers for the preparation of pure water; and vessels of silica probably would be much more suitable for use in exact experiments on the freezing-points and boiling-points of many dilute solutions than the glass-tubes now often used for such work, but of course silica vessels will be very susceptible to the action of alkalis. Finally, vitrified silica may be expected to prove superior to glass for use in researches on pure gases, owing to the qualities of its surface; and for use in experiments concerning the behaviour of gases at high temperatures. We have already one small application of silica to research in this latter field to put upon record.

It is well known that nitrogen and oxygen enter into combination under the influence of the silent discharge, and Sir William Crookes (CHEMICAL NEWS, lxv., 301), has shown that oxides of nitrogen are present in considerable quantities in the flames which accompany the electric discharges of large induction coils. But although various observers have reported indications of the presence of nitrous fumes in the neighbourhood of flames, the forming of an oxide of nitrogen from nitrogen and oxygen alone, and without the intervention of electricity has not, so far as I am aware, been unmistakably established. Therefore it is interesting to record the fact, first observed by my colleague, Mr. Lacell, that nitric peroxide may be produced by heating a mixture of oxygen and nitrogen above the melting-point of platinum in tubes of silica. It is easy to obtain a gas showing a distinctly yellow colour, and exhibiting the reactions of nitric peroxide in this way.

Of course vitreous silica is not entirely without defects. Unfortunately it becomes slightly permeable to hydrogen, as platinum does, though to a less extent, at about 1000° (Villard, *Comptes Rendus*, cxxx., 1752). It is attacked when hot by alkaline oxides. It may be heated to about 960° in contact with copper oxide without injury, but at higher temperatures it is affected. It may be heated more strongly with ferric oxide, but quicklime attacks it at a bright red heat. It is evident that caution must be exercised when it is in contact with basic oxides or alkaline solutions. When one first fashions vessels of silica before the flame the vessels exhibit to a greater or less extent a phenomenon resembling devitrification. They become covered with a white opaque crust. This is easily removed by re-heating, provided that the tube has been kept scrupulously free from dust and dirt during the process of making it. If this precaution has not been taken, the appearance of the vessel may be spoilt permanently. The earlier observers attributed this phenomenon to the volatility of silica. My impression is that it is connected with the minute traces of alkaline metals present in most Brazil pebble, which are usually burnt off in the processes I have described.

From what I have told you to-night you will see that in several respects vitrified silica is as much superior to the best glass as Jena glass is superior to more ordinary specimens, and that the progress made during the last few years will make it possible for investigators to employ vitreous silica much more widely in the future than has been possible in the past. At the same time it is evident that the method of producing it is still in its infancy, that there is much more to be done, and that further progress can only be made at considerable expense.

In concluding my remarks I wish to express the great obligation I am under to my friend and colleague Mr. H. G. Lacell. You will have discovered for yourselves that the chief burden has been upon his shoulders to-night, and that without the illumination provided by his precise and beautiful manipulations my discourse would have been but a dry affair. Also I must add that the cost of the work at its later stages has been aided by a subsidy from the Government Grant Fund of the Royal Society.

THE TITRATION OF A SOLUTION OF HYPOSULPHITE.

By M. PERRIN.

THE exact titration of a solution of hyposulphite by means of a known weight of pure iodine is a complicated and inconvenient method. It is necessary first to sublime the iodine several times, and then to admit that it is absolutely pure; at the same time it must be remembered that the weighing of such a volatile body is itself a very delicate operation.

A much more practical method of titrating hyposulphite consists of using a titrated solution of sulphuric acid, such as is to be found in every laboratory, or even a titrated solution of any acid.

We well know that most acids react on a mixture of iodate and iodide of potassium according to the equation $5KI+IO_3K+3SO_4H_2=3SO_4K_2+3H_2O+I_6$. So that 49 of SO_4H_2 correspond to 127 of iodine.

Method of Operating.

Suppose we wish to make a N/20 solution hyposulphite, we place in a 250 c.c. flask, having a ground glass stopper, about 2 grms. of accurately neutralised iodide of potassium, 50 c.c. of distilled water, and a pinch of pure iodate of potassium; we then add 10 c.c. of an exactly decinormal solution of sulphuric acid. After a few moments we add, drop by drop, the hyposulphite solution to be titrated until all the iodine is transformed; this can be determined by the disappearance of the yellow colour, or by using starch emulsion. In the case where we have used 10 c.c. of decinormal acid we ought to add 20 c.c. of hyposulphite if the latter is N/20.

The only important condition to remember is to use only absolutely neutral iodide of potassium and hyposulphite, but the method would appear to be inapplicable when we have need of an alkaline solution of hyposulphite, for keeping for example.

To overcome this difficulty all we need do after having determined, on the neutral solution of hyposulphite, the quantity of liquid necessary to bring the latter to the desired strength, is to add the difference between the volume of the alkaline solution to be used and that found by calculation.

Let us suppose, for example, that after a preliminary trial, effected on the still neutral solution of hyposulphite, we calculated that it was necessary to add 150 c.c. to obtain a N/20 solution; if, on the other hand, this ought to contain, when once adjusted, 200 c.c. of an alkaline solution, we should only add 130 c.c. of distilled water, and

calculate, if necessary, the number of c.c. and tenths of c.c. which would be required by 10 c.c. of N/10 SO_4H_2 when operating on the solution thus diluted. If the figure previously determined is obtained, nothing remains but to add the alkaline solution.—*Moniteur Scientifique*, April, 1901, p. 244.

ACTION OF PEROXIDE OF HYDROGEN ON THE BLOOD. EASY MEANS OF DISTINGUISHING HUMAN BLOOD FROM THAT OF ANIMALS.

By S. COTTON.

THE well-known property possessed by blood of whatever origin of decomposing peroxide of hydrogen has not yet been examined, so far as I am aware, from the point of view of the volume of oxygen set at liberty. This is what I have now undertaken.

Experimental Method.

The blood is strongly squeezed in a linen bag until nothing remains but the fibrine; we thus get the serum and the corpuscles free from fibrine. After having well stirred the liquid to make it homogeneous I measured out 1 c.c. in a small wide-mouthed flask.

At the same time I placed 250 c.c. of commercial peroxide of hydrogen at 12 vols. in a litre flask.

On account of the necessity of pouring from one flask to another the peroxide is reduced to about 11 vols. Care must be taken, that no bubbles of gas are given off,

The flask containing the blood is then gently dropped into the larger flask and the cork immediately inserted.

The gas is rapidly given off and collected under water, and measured. The operation takes less than an hour.

Results Obtained (Means).

	One c.c. of blood gave:—	
	Maximum.	Minimum.
	C.c.	C c.
Man	610	580
Horse	350	320
Pig	350	320
Bullock	170	165
Guinea-pig	125	115
Sheep	65	60

There is a slight difference in favour of females and the young. This difference would be still more pronounced if we take account of the number of the corpuscles. This is a proof that the quality has more influence than the quantity, since, according to different writers, the blood of the male is richer in corpuscles than that of the female.

To get the most sensitive reaction it is preferable not to operate on more than 1 c.c. of blood, as the first volumes of oxygen are given off more easily than the others; the strength of each variety of corpuscle can be measured with greater distinctness. Further, when reduced to such simplicity the method may be used clinically.

Doubtless, in fact, the above figures would be notably modified by serious illnesses, especially by those in which a micro-organism attacks the corpuscles, such as in malaria, anthrax, or in leucocythenia.

The addition of water rapidly decreases the decomposing power; 7 vols. of water added to 1 vol. of blood reduced the gas given off by human blood from 600 to 65 c.c. This should make an interesting subject of research.

Theoretically, also, we might expect to find greater variations with peroxide of hydrogen of higher tension. This decomposing property goes on increasing in the case of human blood during the first six hours of its exposure to air, as if the corpuscles required to be supersaturated with oxygen. It then remains stationary for twelve or fourteen hours according to the temperature, that is so long as the temperature does not vary. It then decreases, without, however, reaching zero. The blood of animals shows this in a much more rapid and less durable manner.

Peroxide of hydrogen acts on the blood, not as on permanganates, which are only incompletely reduced, but rather in the same manner as on iodic acid; the reduction is complete, the corpuscle is entirely destroyed and decolourised. It loses the whole of its oxygen, while the peroxide loses only a portion.

We can also compare this action to that which it exerts on ferments and microbes.

The albumin of the serum has no action. The fibrine, in spite of what has been said, only acts very slightly when it has been really freed from hæmoglobin.

The deductions to be drawn from these observations are the following.—

1. Human blood has a much stronger decomposing action on peroxide of hydrogen than that of animals. The volume of gas given off is more than four times the amount than in the case of bullock's blood, and ten times greater than with sheep's blood.

2. It should on this account be extremely easy to distinguish between human blood and that of animals.

3. The blood of animals transfused to a man would asphyxiate the latter. The same would occur between animals of different species. This may be looked upon as a new line of distinction as important as the one already recognised by Cuvier.

4. Microbes which are pathogenic to man, in whom they reach their maximum development when transferred to the blood of animals, where the vital conditions are so different, become weakened themselves through partial asphyxia, and lose a part of their activity; that is to say, their virulence. This is the secret of attenuated serums and viruses.—*Bull. Soc. Chim.*, Series 3, vol. xxv., No. 5.

THE MOLECULAR WEIGHT OF ALUMINIUM COMPOUNDS.*

By ELMER P. KOHLER.

(Concluded from p. 195).

III. ADDITION PRODUCTS.

ALUMINIUM bromide, like aluminium chloride, combines directly with acid chlorides, ketones, esters, nitro-compounds, and tertiary amines. The compounds obtained with the bromide are invariably more easily soluble in carbon disulphide than those obtained with the chloride. It is therefore easier to get them in a form in which it is possible to use them for molecular weight work. They are, at best, extremely difficult to manipulate, and only very few gave satisfactory results. With these, however, it was possible to prove that, for the purpose of this investigation, it is not at all necessary to isolate the substances. They can just as well be made in the apparatus in which their molecular weight is to be determined.

Benzene Sulphonchloride and Aluminium Bromide.

Slightly more than two molecules of pure benzene sulphonchloride were added to one molecule of aluminium bromide dissolved in a large amount of carbon disulphide. The flask was closed with a phosphorus pentoxide tube, and the disulphide allowed to evaporate slowly through the tube. In the course of a week the product began to separate in large colourless tables. The solution was removed in a current of dry air, the crystals washed with dry disulphide, dried in a current of dry air, and used without further purification. A halogen determination gave the following results:—

I. 0·3245 grm. substance gave 0·5152 grm. silver halide.
II. 0·4105 „ „ 0·6530 „ „

* From the *American Chemical Journal*, xxiv., No. 5.

	Calculated for $(AlBr_3.C_6H_5SO_2Cl)_x$.	Found. I.	Found. II.
Cl,Br	62·07	61·8	61·9

Molecular Weight of $(AlBr_3.C_6H_5SO_2Cl)_x$.

Solvent: Carbon disulphide. K=2370.

	Solvent. Grms.	Substance. Grms.	Rise in boiling-point.	Molecular weight.
1.	40·1110	1·0030	0·086	899
2.	40·1110	1·9230	0·128	887
3.	40 1110	3·1255	0·210	879
4.	40·1110	3·7110	0·244	898
	Mean			890·75
	Calculated for $Al_2Br_6.2C_6H_5SO_2Cl$.			887·08

Nitrobenzene and Aluminium Bromide.

Gatterman (*Ber. d. Deut. Chem. Ges.*, xii., 2719) found that aluminium chloride combines with nitrobenzene to form a crystalline addition-product of the composition $AlCl_3.C_6H_5NO_2$. The corresponding aluminium bromide compound crystallises well at low temperatures, forming large yellow prisms considerably less sensitive to atmospheric moisture than the analogous addition-products with acid chlorides. The substance was washed with dry carbon disulphide and dried in a current of air.

Molecular Weight of $(AlBr_3.C_6H_5NO_2)_x$.

Solvent: Carbon disulphide. K = 2370.

	Solvent. Grms.	Substance. Grms.	Rise in boiling-point.	Molecular weight.
1.	40·2020	0·8510	0 064	784
2.	40·2020	1·8200	0·135	794
3.	40·2020	2·3840	0·178	789
4.	40·2020	2·9630	0·220	794
	Mean			790·25
	Calculated for $Al_2Br_6.2C_6H_5NO_2$ ..			780·14

According to these results, one molecule of aluminium bromide combines with two molecules of other substances to form one molecule of product:—

$$Al_2Br_6+2C_6H_5SO_2Cl=Al_2Br_6.2C_6H_5SO_2Cl,$$
$$Al_2Br_6+2C_6H_5NO_2=Al_2Br_6.2C_6H_5NO_2.$$

If these equations are correct, then the addition of sulphonchloride or nitro-compound to a solution of aluminium bromide of known boiling-point should not affect the boiling-point so long as the bromide is in excess; while the addition of the bromide to a solution of benzene sulphonchloride or nitrobenzene should immediately lower the boiling-point, and the lowering should be proportional to the grm.-molecular amounts of bromide added. The experimental results are as follows:—

Effect of Adding Benzene Sulphonchloride to a Solution of Aluminium Bromide.

Solvent: Carbon disulphide. K = 2370.

	Solvent. Grms.	Bromide. Grms.	Sulphonchloride. Grms.	Boiling-point.	Change in boiling-point.
1.	39·7150	—	—	2·572	—
2.	39·7150	1·7730	—	2·770	0·198
3.	39·7150	1·7730	0·2335	2·770	0·000
4.	39·7150	1·7730	0 6980	2·770	0·000
5.	39·7150	1·7730	1·1840	2·810	0·040

The weight of sulphonchloride equivalent to 1·7730 grms. aluminium bromide is 1·1749 grms.; the amount added is 1·1840 grms.; the elevation of the boiling-point calculated for the difference, assuming—what is only approximately true—that the constant for the solution is the same as that for the pure solvent, is 0·045; the elevation found is 0·040.

Effect of Adding Aluminium Bromide to a Solution of Benzene Sulphonchloride.

	Solvent. Grms.	Sulphonchloride. Grms.	Bromide. Grms.	Boiling-point.	Change in boiling-point
1.	41·8860	—	—	2·590	—
2.	41·8860	2·5150	—	3·394	+0·804
3.	41·8860	2·5150	0·5050	3·342	−0·052
4.	41·8860	2·5150	1·3800	3·247	−0·142
5.	41·8860	2·5150	2·5950	3·118	−0·275

The molecular weight of aluminium bromide calculated from these lowerings, assuming K=2370, is as follows:—

	Solvent. Grms.	Bromide. Grms.	Lowering of boiling-point.	Molecular weight.
1.	41·8860	0·5050	0·052	560
2.	41·8860	1·3800	0·142	548
3.	41·8860	2·5950	0·275	536
	Calculated for Al_2Br_6			534

No better proof of the formula Al_2Br_6 seems possible. No other assumption would explain these results. It will be observed that the error introduced by the presence of the sulphonchloride is small in comparison with the normal error of these determinations, which is unavoidably large, partly owing to the sensitiveness of the substances and partly to their great molecular weight. Knowing that aluminium chloride combines with nitrobenzene to form a compound $(AlCl_3.C_6H_5NO_2)_x$, it is possible to determine whether the formula of the chloride is analogous to that of the bromide or not.

Aluminium Chloride and Nitrobenzene.

Solvent: Carbon disulphide. K = 2370.

	Solvent. Grms.	Nitrobenzene. Grms.	Chloride. Grms.	Lowering of boiling-point.	Molecular weight.
1.	40·2250	2·1310	0·8250	0·170	284
2.	40·2250	2·1310	1·4355	0·308	275
3.	40·2250	2·1310	2·0310	0·444	270
	Mean				276·33
	Calculated for Al_2Cl_6				266·9

The facts established up to this point supply an elegant method for determining what happens when an aluminium halide is brought in contact with a given substance in an indifferent medium. It is sufficient for this purpose to prepare a solution of aluminium bromide, of known concentration and boiling-point, to add to this successive portions of the substance under investigation until it is present in excess, and then add a fresh portion of aluminium bromide. The thermometer readings after each addition of material, give an accurate account of what goes on in the solution. The following results were obtained in this way:—

Aluminium Bromide and Benzoyl Chloride.

The calculations are based on the equation—

$$Al_2Br_6+2C_6H_5COCl=Al_2Br_6.2C_6H_5COCl.$$

Solvent: Carbon disulphide. K=2370.

	Solvent. Grms.	Bromide. Grms.	Chloride. Grms.	Change in boiling-point.	Calculated change in boiling-point.
1.	38·1500	1·7140	—	+0·020	+0·0215
2.	38·1500	1·7140	0·3370	0·000	0·000
3.	38·1500	1·7140	0·9460	0·000	0·000
4.	38·1500	1·7140	1·2380	+0·128	+0·130
5.	38·1500	2·2670	1·2380	−0·053	−0·054

Aluminium Bromide and Benzophenone.

The calculations are based on the equation—

$$Al_2Br_6+2C_6H_5COC_6H_5=Al_2Br_6.2C_6H_5COC_6H_5.$$

	Solvent. Grms.	Bromide. Grms.	Ketone. Grms.	Change in boiling-point.	Calculated change in boiling-point.
1.	40·1510	1·1010	—	+0·118	+0·121
2.	40·1510	1·1010	0·4117	0·000	0·000
3.	40·1510	1·1010	1·3290	+0·211	+0·213
4.	40·1510	1·6120	1·3290	−0·054	−0·057

Aluminium Bromide and Phosphorus Oxychloride.

The calculations are based on the equation—

$$Al_2Br_6 + 2POCl_3 = Al_2Br_6.2POCl_3.$$

	Solvent. Grms.	Bromide. Grms.	Oxychloride. Grms.	Change in boiling-point.	Calculated change in boiling-point.
1.	40·2150	1·3520	—	+0·147	+0·150
2.	40·2150	1·3520	0·6772	0·000	0 000
3.	40·2150	1·3520	1·2282	0·172	+0·173
4.	40·2150	1·8070	1·2282	−0·047	−0 050

Aluminium Bromide and Dibrombenzene (p).

The Friedel and Crafts reaction is not applicable to dihalogen compounds. The experiment was made to determine whether this is due to a combination of the halogen compound with the aluminium halide. The results show that this is not the case. The calculations are based on the assumption that both substances are present unchanged:—

	Solvent. Grms.	Bromide. Grms.	Dibrom-benzene. Grms.	Rise in boiling-point.	Molecular weight.
1.	40·6650	1·7000	—	0·186	533
2.	40·6650	1·7000	0·5860	0·140	244
3.	40·6650	1·7000	1·4400	0 340	246
4.	40·6650	1·7000	2·2040	0·540	240
5.	40·6650	2 8050	2·2040	0·120	540

Calculated for Al_2Br_6	534
Calculated for $C_6H_4Br_2$	236

Of other substances examined, acetophenone benzene sulphonacetone, and ethyl benzoate form addition-products with aluminium halides, and behave like benzophenone. Benzene and naphthalene give results like those of dibrombenzene, but they slowly react to form insoluble compounds. Pyridine and quinoline form crystalline addition-products insoluble in carbon disulphide.

The results thus far given show conclusively that in an indifferent medium the aluminium halides form addition-products that are not measurably dissociated. The results are quite different when a large excess of one of the components is present. It was shown above that, in carbon disulphide, aluminium bromide combines with nitrobenzene to form a compound of the formula $Al_2Br_6.2C_6H_5NO_2$. If this compound, or aluminium bromide itself, is dissolved in nitrobenzene and the lowering of the freezing-point of the latter measured, the results lead to a much simpler formula.

Aluminium Bromide in Nitrobenzene.

K = 7070.

	Nitrobenzene. Grms.	Bromide. Grms.	Lowering of freezing-point.	Molecular weight.
1.	15·2470	1·2530	2·11	275·5
2.	15·2470	1·9040	3·20	276·0
3.	15·2470	2·4250	4·08	277·0
	Mean			276·17
	Calculated for $AlBr_3$			267

Aluminium Chloride in Nitrobenzene.

K = 7070.

	Nitrobenzene. Grms.	Chloride. Grm.	Lowering of freezing-point.	Molecular weight.
1.	19·7640	0·1893	0·520	130·4
2.	19·7640	0·5953	1·675	127·5
3.	19·7640	0·8923	2·500	131·0
	Mean			129·63
	Calculated for $AlCl_3$			133·4

The results are exactly like those obtained in pyridine solution. As a mean of six determinations of the molecular weight of aluminium chloride in pyridine, Werner and Schmujlow obtained the value 129 6, and Werner concludes that $AlCl_3$ is the only formula permissible. The conclusion is not justified. Pyridine combines with aluminium chloride to form a well-crystallised compound, and there is no experimental evidence that molecular weight determinations, made in solvents that combine with the substance under investigation, are trustworthy. In aqueous solutions they are not, and my results show that they are equally unreliable in this case. Between the results in carbon disulphide and those in nitrobenzene or pyridine, it is easy to decide by the aid of the following considerations:—In the absence of any solvent, benzoyl chloride combines with aluminium bromide to form a well-crystallised compound which, as shown by analysis, has the composition $(AlBr_3.C_6H_5COCl)_x$. The molecular weight must, therefore, correspond to some multiple of this formula. The determination in carbon disulphide gave a value corresponding to the double formula—

$$(AlBr_3.C_6H_5COCl)_2$$

—a possible value. The determination in nitrobenzene gives an impossible value—

$$(AlBr_3.C_6H_5COCl)_x.$$

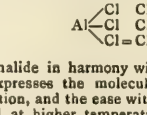
Solvent: Nitrobenzene. K = 7070.

	Solvent. Grms.	Substance. Grms.	Lowering of freezing-point.	Molecular weight.
1.	20·2500	0·5820	0·424	371
2.	20·2500	1·0105	0·952	370
3.	20·2500	1·8200	1·710	371

Calculated for $(AlBr_3.C_6H_5COCl)_x$, $(407·5)_x$.

It is evident from these results that nearly all the values for inorganic salts obtained by Werner and his pupils will need re-determination, since they purposely selected solvents that combine with salts and in many cases proved combination by isolating the products. The same is true of the determinations made by Lespeau (*Bull. Soc. Chim.*, [3], xvii., 934) in ether, and those by Rosenheim and Woge (*Zeit. Anorg. Chem.*, xv., 283) in pyridine.

The principal objections to the double formulæ for the aluminium halides have been based on the assumption that these formulæ imply quadrivalent aluminium (Erdman, "Lehrbuch d. Anorg. Chem.," 587). To avoid this, Traube (*Ber. d. Deut. Chem. Ges.*, xxv., 1716) assumed that these salts are derived from an hexavalent complex of two aluminium atoms, $[Al{\equiv}Al]^{VI}$. Neither of these assumptions is necessary. The aluminium halides behave like typical double halides with the formula $^{III}\ \ ^{III}\ \ \ ^{III}\ \ ^{III}$ $AlCl_3.Cl_3Al$ or the formula $(AlX_6)Al$. Their behaviour in nitrobenzene and pyridine, moreover, makes it fairly certain that no double molecules are present in aqueous solution. The hydrous salt that crystallises out of aqueous solutions is probably $AlCl_3.6H_2O$. The anhydrous salt is probably—



a double halide in harmony with Remsen's law.* The formula expresses the molecular weight, the power of direct addition, and the ease with which the substance is dissociated at higher temperatures and in solution. In any case, I believe that the matter can be reached by experiment, and the work will be continued in this direction and extended to include the compounds of iron.

* This formula is essentially the same as that used by Remsen (*Am. Chem. Journ.*, xi., 316) to account for the peculiar results obtained in the determination of the vapour-density of aluminium chloride.

SOME PRINCIPLES AND METHODS OF ROCK ANALYSIS.*

By W. F. HILLEBRAND.

(Continued from p. 196).

XVIII. *Vanadium (Chromium) and Molybdenum. Distribution of Vanadium and Molybdenum.*

THE wide distribution of vanadium throughout the earth's crust has in recent years been clearly established (see *ante*, p. 67), not only in ores and in coals, but in clays, limestones, sandstones, and igneous rocks.† The writer has shown (*loc. cit.*) that vanadium occurs in quite appreciable amounts in the more basic igneous and metamorphic rocks up to 0·08 per cent or more of V_2O_3, but that it seems to be absent or nearly so, from the highly siliceous ones. Some of their ferric aluminous silicate constituents carry still higher percentages—up to 0·13 per cent V_2O_3 in a biotite separated from a pyroxenic gneiss. Molybdenum, on the other hand, appears to be confined in quantities susceptible of detection to the more siliceous rocks, and, except perhaps in rare instances, is not present in them in quantitatively determinable amount when operating on 5 grms. of material. Hence the quantitative search for vanadium will usually be limited to rocks with less than 60 per cent of silica. The search for it even then will perhaps not often warrant the necessary expenditure of time, but in this connection it is to be remembered that neglect to estimate it introduces an error in the figures for both ferrous and ferric oxides, which in extreme cases met with may be of considerable moment. (See p. 151, and also *prox*).

Description of Method.

In the following method there is nothing absolutely novel except that chromium and vanadium, when together, need not be separated, but are determined, the former colorimetrically, as already described (p. 195), the latter volumetrically, in the same solution. (W. F. Hillebrand, *Journ. Am. Chem. Soc.*, 1898, vol. xx., p. 461; CHEMICAL NEWS, 1898, vol. lxxviii., p. 295; *Bull. U.S. Geol. Survey*, No. 167, p. 44).

Five grms. of the rock are thoroughly fused over the blast with 20 of sodium carbonate and 3 of sodium nitrate. After extracting with water and reducing manganese with alcohol, it is probably quite unnecessary, if the fusion has been thorough, to re-melt the residue as above, though for some magnetites and other ores containing larger amounts of vanadium than the generality of rocks, this may be necessary, as Edo Claassen has shown (*Am. Chem. Journ.*, 1886, vol. viii., p. 437). The aqueous extract is next nearly neutralised by nitric acid, the amount to be used having been conveniently ascertained by a blank test with exactly 20 grms. of sodium carbonate, &c., and the solution is evaporated to approximate dryness. Care should be taken to avoid overrunning neutrality, because of the reducing action of the nitrous acid set free from the nitrite produced during fusion, but when chromium is present it has been my experience that some of this will invariably be retained by the precipitated silica and alumina, though only in one case have I observed a retention of vanadium, it being then large. The use of ammonium nitrate instead of nitric acid for converting the sodium carbonate into nitrate does not seem to lessen the amount of chromium retained by the silica and alumina.

As a precautionary measure, therefore, and always when chromium is to be estimated also, the silica and alumina precipitate should be evaporated with hydrofluoric and sulphuric acids, the residue fused with a little sodium carbonate, and the aqueous extract again nearly neutralised with nitric acid and boiled for a few moments, the filtrate being added to the main one.

Mercurous nitrate is now added to the cold alkaline solution in some quantity, so as to obtain a precipitate of considerable bulk, containing, besides mercurous carbonate, chromium, vanadium, molybdenum, tungsten, phosphorus, and arsenic, should all happen to be in the rock. The mercurous carbonate serves to counteract any acidity resulting from the decomposition of the mercurous nitrate. Precipitating in a slightly alkaline instead of a neutral solution renders the addition of precipitated mercuric oxide unnecessary for correcting this acidity. If the alkalinity, as shown by the formation of an unduly large precipitate, should have been too great, it may be reduced by careful addition of nitric acid until an added drop of mercurous nitrate no longer produces a cloud.

After heating and filtering, the precipitate is ignited in a platinum crucible, after drying and removing from the paper to obviate any chance of loss of molybdenum and of injury to the crucible by reduction of arsenic. The residue is fused with a very little sodium carbonate, leached with water, and the solution, if coloured yellow, filtered into a graduated flask of 25 or more c.c. capacity. The chromium is then estimated accurately in a few minutes by comparing with a standard alkaline solution of potassium monochromate (p. 196). Then, or earlier in absence of chromium, sulphuric acid is added in slight excess, and molybdenum and arsenic, together with occasional traces of platinum, are precipitated by hydrogen sulphide, preferably in a small pressure bottle.* If the colour of the precipitate indicates absence of arsenic the filter with its contents is carefully ignited in porcelain, and the delicate sulphuric-acid test for molybdenum is applied as follows:—The molybdenum compound is heated in porcelain with a single drop of strong sulphuric acid till the acid is nearly volatilised. On cooling a beautiful blue colour is proof of the presence of molybdenum.

The filtrate, in bulk from 25 c.m.³ to 100 c.m.³ is boiled to expel hydrogen sulphide, and titrated at a temperature of 70° to 80° C. with a very dilute solution of permanganate representing about 1 m.grm. of V_2O_5 per c.c. as calculated from the iron strength of the permanganate, one molecule of V_2O_5 being indicated for each one of Fe_2O_3. One or two checks are always to be made by reducing again by means of a current of sulphur dioxide gas, boiling this out again,† and repeating the titration. The latter results are apt to be a very little lower than the first, and are to be taken as the correct ones.

In case the volume of permanganate used is so small as to make doubtful the presence of vanadium, it is necessary to apply a qualitative test, which is best made as follows:—The solution is evaporated and heated to expel excess of sulphuric acid, the residue is taken up with 2 or 3 c.c. of water, and a few drops of dilute nitric acid, and a couple of drops of hydrogen peroxide are added. A characteristic brownish tint indicates vanadium. Unless the greater part of the free sulphuric acid has been removed the appearance of this colour is sometimes not immediate and pronounced, hence the above precaution. It is also necessary that the nitric acid shall be in considerable excess, since in a neutral or only faintly acid solution the colour does not appear strongly.

The above is a surer test to apply than the following:—Reduce the bulk to about 10 c.c., add ammonia in excess,

* *Bulletin of the United States Geological Survey*, No. 176.

† W. F. Hillebrand, "Distribution and Quantitative Occurrence of Vanadium and Molybdenum in Rocks of the United States." *Amer. Journ. Sci.*, 1898, 4th Ser., vol. vi., p. 209; CHEM. NEWS, 1898, vol. lxxviii., p. 216; *Bull. U.S. Geol. Survey*, No. 167, p. 49.

* From a sulphuric solution the separation of platinum and molybdenum by hydrogen sulphide is much more rapid and satisfactory than from a hydrochloric solution.

† The direct use of a solution of sulphur dioxide or of an alkali sulphite is inadmissible unless these have been freshly prepared, since after a lapse of time they contain other oxidisable bodies than sulphurous acid or a sulphite. The sulphur dioxide is best obtained as wanted by heating a flask containing a solution of sulphur dioxide, or of a sulphite to which sulphuric acid has been added. The expulsion of the last traces of sulphur dioxide is said to be more effectively accomplished by boiling with simultaneous passage of a rapid current of carbon dioxide for a few minutes at the last than by boiling alone. Because of the small amount of air carried with it, long passage of the gas is said to result in slight oxidation of the vanadium (Manasse, *Ann. Chem. u. Pharm.*, 1887, vol. ccxl., p. 23; *Zeit. fur Anal. Chemie*, 1893, vol. xxxii., p. 225).

and introduce hydrogen sulphide to saturation. The beautiful cherry-red colour of vanadium in ammonium-sulphide solution is much more intense than that caused by hydrogen peroxide in acid solution, but the action of ammonia is to precipitate part or all of the vanadium with the chromium or aluminum that may be present or with the manganese used in titrating, and ammonium sulphide is unable to extract the vanadium wholly from these combinations. Usually, however, the solution will show some colouration, and addition of an acid precipitates brown vanadium sulphide, which can be collected, ignited, and further tested if desired.

Application of the Method in presence of Relatively much Chromium.

The application of the method in its foregoing simplest form is subject to one limitation—the chromium must not be present above a certain moderate amount. This limitation is due to the considerable amount of permanganate then required to produce a clear transition tint when titrating in a hot solution, as is advisable with vanadium. In a cold solution of chromic sulphate much less permanganate is needed to produce the peculiar blackish tint without a shade of green, which affords a sure indication of excess of permanganate, but in a hot and especially a boiling solution the oxidation of the chromium itself takes place so rapidly that a very large excess of the reagent may be added before a pronounced end reaction is obtained. Nevertheless, quite satisfactory determinations of as little as 1 or 2 m.grms. of vanadium pentoxide can be made in presence of as much as 30 m.grms. of chromic oxide. To accomplish this it is only necessary to apply a simple correction obtained by adding permanganate to a like bulk of equally hot chromic sulphate solution containing approximately the same amount of chromium.

Ridsdale (*Journ. Chem. Soc.*, 1888, vol. vii., p. 73), titrated the cold solution to avoid oxidation of chromium, and obtained accurate results, but in the writer's experience the end reaction is then uncertain.

Tables V. and VI. contain the results of a considerable number of tests, those in Table VI. being tabulated separately in order to show the degree of accuracy attainable with a large excess of chromium by applying the correction above mentioned and also the amount of this correction.

In spite of the fact that the correction in most of the trials of Table VI. represents a large proportion of the permanganate used, the results must be considered satisfactory in view of the small amount of vanadium present, and they show that the method in competent hands after a little experience affords trustworthy figures.

The method of T. Fischer ("Inaugural Dissertation," Rostock, 1894)—digestion of the precipitated lead salts with a strong solution of potassium carbonate—appears to offer the long-needed satisfactory quantitative separation of arsenic, phosphorus, chromium, tungsten, and molybdenum from vanadium, the normal lead meta-vanadate remaining quite unattacked, according to the author, while the other lead salts are wholly decomposed, but the applicability of this method to the separation of the minute amounts often found in rocks and ores has not been tested. The object has been in the present case to reach satisfactory results with the greatest expedition, and when chromium is not present in considerable amount this is accomplished.

Fortunately, chromium is almost never a prominent constituent of clays, coals, iron ores, and those rocks in which vanadium has thus far been reported, for although it is usually certain of the most basic of the silicate rocks that are highest in chromium—as the peridotites—yet in these, so far as present experience teaches, vanadium is lacking, a fact doubtless connected with the simultaneous absence from them of ferric-aluminous silicates.

Condition of Vanadium in Rocks.

The above and elsewhere mentioned connection of vanadium with the ferric-aluminous silicates of rocks,

TABLE V.—*Tests for Vanadium in the presence of Chromium.*

No.	Chromic oxide.	Vanadium pentoxide.	Vanadium pentoxide found.	Error.
	M.grms.	M.grms.	M.grms.	M.grm.
1.	1	0·87	0·22	−0·15
2.	1	0·94	1·04	+0·10
			0·98	+0·04
3.	1·5	5·25	5·49	+0·24
			5·43	+0·19
4.	2	5·62	5·5	−0·12
			5·5	−0·12
5.	3	4·68	4·78	+0·10
			4·78	+0·10
			4·83	+0·15
6.	3	5·62	5·58	−0·04
			5·58	−0·04
7.	3·5	18·74	18·89	+0·15
			18·97	+0·23
8.	6	5 6	6·1	+0·50
9.	6	4·68	4·78	+0·10
10.	6	5·62	5·58	−0·04
11.	10	5·62	5·58	−0·04
12.	10	23·52	23·81	+0·29
			23·71	+0·19
13.	10	46·85	46·98	+0·13
			47·20	+0·35
14.	25	23·52	23·65	+0·13
			23·75	+0·23
15.	87·5	23·52	23·71	+0·19

TABLE VI.—*Showing Application of Correction for Larger Amounts of Chromium, obtained by Adding Potassium Permanganate to an Equal Bulk of Solution containing a Like Amount of Chromic Sulphate.*

No.	Chromic oxide.	Vanadium pentoxide.	Vanadium pentoxide found. Uncorrected.	Vanadium pentoxide found. Corrected.	Error.	Volume of solution.
	M.grms.	M.grms.			M.grm.	C.m.s.
16.	20	0·94	1·59	0·99	+0·05	50—100
17.	20	1·87	2·69	2·09	+0·22	50—100
			2·39	1·79	−0·08	
			2·59	1·99	+0·12	
18.	20	18·74	19·4	18·73	−0·01	50—100
			19·3	18·63	−0·11	
			19·3	18·63	−0·11	
19.	30	1·87	2·99	2·14	+0·27	About 100
			2·79	1·94	+0 07	
			2·79	1·94	+0·07	
			2·69	1·84	−0·03	
			2·69	1·84	−0·03	
20.	30	1·87	2·69	1·79	−0·08	200
			2·89	2·09	+0·22	
			2·89	2·09	+0·22	
			2·79	1·99	+0·12	
21.	62	46·85	48·60	47·60	+0·75	200

taken in connection with the existence of the mineral roscoelite, classed as a vanadium mica, indicates a condition of the vanadium corresponding to aluminum and ferric iron, and that it is to be regarded as replacing one or both of these elements. Hence it should be reported as V_2O_3 and not as V_2O_5.

What its condition may be in matter of secondary origin, like clays, limestones, sandstones, coals, and ores of iron, is yet open to discussion. It was the writer's opinion until recently that it should then be regarded as in the pentavalent state (V_2O_5), but his work upon certain remarkable vanadiferous sandstones (Hillebrand and Ransome, *Amer. Journ. Sci.*, 1900, Fourth Series, vol. x., p. 120), of Western Colorado, in which it unquestionably occurs as trivalent vanadium (V_2O_3), has led to a decided unsettling of this view. It is but proper to recall that Czudnowicz (*Pogg. Ann.*, 1863, vol. cxx., p. 20), because of the extreme

difficulty in completely extracting it from iron ores by an alkali-carbonate fusion, and because of the easy reducibility of vanadic acid by ferrous salts, under the conditions in which brown iron ores are supposed to form, considered the vanadium in such ores to be in a lower condition of oxidation (V_2O_3). Lindemann's ("Dissertation," Jena., 1878, through *Zeit. fur Anal. Chemie*, 1879, vol xviii., p. 99), contrary conclusion with regard to certain iron ores, because the vanadium was extracted as V_2O_5 by sodium-carbon fusion without nitre, is not valid, since this would probably be the case even if it existed in the ore as V_2O_3.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, April 18th, 1901.

Prof. Emerson Reynolds, F.R.S., President, in the Chair.

Messrs. B. F. Howard, L. Dobbin, W. H. Oates, and Maj.-Gen. Waterhouse were formally admitted Fellows of the Society.

The following certificates were read for the first time:—Guy Ashwell, Standard Bank, Bulawayo; Thomas Aspinall, 42, Gilnow Road, Bolton; William George Aston, 4, Dalkeith Road, Ilford; Edwin Sloper Beaver, 5, Bonham Terrace, Warminster; Fred Bedford, 9, Market Place, Sleaford, Lincs.; Arthur Crabtree, 9, Bigg Market, Newcastle-on-Tyne; Daniel McLaren, Brookdale, Gray Street, Stalybridge; John Powell, Bailiol House, Wentworth Street, E; John Davidson Spence, 2, Hawkhill Place, Perth Road, Dundee; William Arthur Whitton, Bristol Brewery, Brighton.

The following certificate was authorised by the Council under By-law I. (3):—

Joseph de Verteuil, Clarence Street, Port of Spain, Trinidad, B.W.I.

The following letter has been received from Professor Markownikoff in reply to the letter of congratulation addressed to him by the Council:—

Moscow, 22nd March/4th April.

Dear Sir,—Some years ago I was highly honoured to be received into the list of Foreign Members of the most appreciated Chemical Society of London, and am now deeply moved by the new sign of attention and the hearty congratulations of my dear colleagues.

I beg you to convey to them that devotion to our science will not leave me until the very last.—Your respectful obedient servant,

W. Markownikoff.

Prof. Meldola, Foreign Secretary.

Extraordinary General Meeting.

The President stated that, having received a requisition signed by a sufficient number of Fellows asking that an Extraordinary General Meeting of the Society be called to consider the change of the day and hour of meeting which the Council had decided upon for the ordinary meetings during the ensuing session, he had fixed Wednesday, May 15th, at 8 p.m. for this meeting.

Of the following papers, those marked * were read:—

*55. "*Action of Alkyl Haloids on Aldoximes and Ketoximes.* Part II. *Alkylated Oximes and Isoximes and the Constitution of Aliphates Oximes.*" By W. R. Dunstan and E. Goulding.

In a previous paper (*Trans.*, 1897, lxxi., 573), the authors showed that the direct action of alkyl haloids on aldoximes and ketoximes results in the formation of alkyl nitrogen derivatives only, these being derivatives of the isoximes—

$$RHC{=}NH \quad \text{and} \quad R_2C{=}NH$$
$$\diagdown\!\diagup \qquad\qquad \diagdown\!\diagup$$
$$O \qquad\qquad O$$

When the alkyl haloid acts on the sodium derivatives of the oximes, that is, on the oximes in presence of sodium methoxide, these derivatives of the isoximes are formed, but together with the true ethers of the oximes, RHC:NOH and R_2C:NOH.

The alkyl isoximes are highly unstable, and have been studied chiefly as the compounds they form with sodium iodide. On hydrolysis they furnish the corresponding aldehyde or ketone, together with a β-substituted hydroxylamine. On reduction in the ordinary manner they are converted into the primary amine of the substituted alkyl and the corresponding aldehyde or ketone. By careful reduction with sodium amalgam and acetic acid in alcoholic solution they are changed, by substitution of hydrogen for oxygen, into the corresponding secondary amines. This is a satisfactory method of preparing pure secondary amines.

The alkyl ethers of the oximes are stable liquids. On hydrolysis they furnish the aldehyde or ketone, and an α-substituted hydroxylamine.

Isomeric alkyl derivatives of acetaldoxime, acetoxime, and acetophenoxime were described, and also their hydrolytic and reduction products.

The authors consider that their results support the view that the isoximido-form represents the ordinary structure of the aliphatic oximes, only alkyl nitrogen derivatives being obtained from them by the direct action of alkyl haloids, the hydroxylic structure in the formation of ethers being determined by the formation of the so-called "salts" with highly electro-positive metals. These salts are, however, readily dissociated, so that by acting on them, in alcoholic solution, with the alkyl haloid, some alkyl isoxime is always formed from the free oxime present.

*56. "*The Supposed Existence of Two Isomeric Triethyloxamines.*" By W. R. Dunstan and E. Goulding.

The triethyloxamine, $(C_2H_5)_3NO$, obtained by the authors (*Trans.*, 1899, lxxv., 792, and *Trans.*, 1900, lxxvii., 1006), was shown to possess properties which differ from those of the compound described by Bewad, to which he assigned the same constitution. This difference has been since investigated and confirmed by Lachman (*Ber.*, 1900, xxxiii., 1022), who, however, was unable to offer any explanation of it. The question is now settled by the observation that the compound described by Bewad is in reality β ethyl-*sec*-butylhydroxylamine, as Bewad himself has shown (*Journ. Russ. Phys. Chem.*, 1900, xxxii., 455). The triethyloxamine obtained by the authors is at present therefore the only known compound having this constitution.

*57. "*Nitrocamphene, Aminocamphene, and Hydroxycamphene.*" By M. O. Forster.

1-*Nitrocamphene*,—

$$C_8H_{14}\begin{cases}\text{CH}\\ \|\\ \text{C·NO}_2\end{cases},$$

prepared by heating an alcoholic solution of 1 : 1-bromonitrocamphane with silver nitrate, crystallises from alcohol in long, hard, striated prisms, and melts at 56°; it has $[\alpha]_D = +112{\cdot}0°$ in alcohol, and $+137{\cdot}5°$ in benzene. 2 : 1-*Bromonitrocamphane*,—

$$C_8H_{14}\begin{cases}\text{CHBr}\\ |\\ \text{CH·NO}_2\end{cases},$$

obtained when nitrocamphene is treated with hydrobromic acid, crystallises from alcohol, and melts at 178°. 1 : 2-*Dibromo*-1-*nitrocamphane*,—

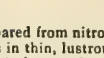
$$C_8H_{14}\begin{cases}\text{CHBr}\\ |\\ \text{CBr·NO}_2\end{cases},$$

produced by the action of bromine on nitrocamphene,

crystallises in long, flat, transparent needles, and melts at 195°. 2 : 1-*Iodonitrocamphane*,—

prepared from nitrocamphene and hydriodic acid, crystallises in thin, lustrous plates, and melts at 118°.

1-*Aminocamphene*,—



formed on reducing nitrocamphene with zinc dust and glacial acetic acid, melts at 46°, and boils at 191—192° under 758 m.m. pressure; it has $[\alpha]_D = +59{\cdot}7°$ in alcohol. The *sulphate*, *picrate*, *platinichloride*, and the *benzoyl*, *benzylidene*, and *phenylcarbamide* derivatives are well-defined.

1-*Hydroxycamphene*,—

obtained on heating aminocamphene sulphate with potassium nitrite, crystallises in long needles, melts at 74°, and boils at 212° under 750 m.m. pressure; it has $[\alpha]_D = +34{\cdot}1°$ in absolute alcohol. Hydroxycamphene is indifferent towards alkalis, but warm dilute mineral acids transform it immediately into ordinary camphor.

58. "*A Contribution to the Chemistry of the Triazoles.*" By G. Young and W. H. Oates.

The authors discuss the possibility of isomerism in the triazole series as compared with the pyrazoles.

The following compounds have been obtained :—

Benzal-2-methylsemicarbazone,—

$$C_6H_5{\cdot}CH{:}N{\cdot}N(CH_3){\cdot}CO{\cdot}NH_2,$$

m. p. 159—160°; 3-*phenyl*-1-*methylhydroxytriazole*,—

m. p. 218—219°; *acetyl* derivative, m. p. 72·5—73°; *silver* derivative, $C_9H_8ON_3Ag$; 3 *phenyltriazole*, m. p. 118·5—119°; *cinnamal-2-methylsemicarbazone*, m. p. 155°; *strenylmethylhydroxytriazole*, m. p. 204—205°; *silver* derivative, $C_{11}H_{10}ON_3Ag$; *acetyl* derivative, m. p. 88—89°; *m-nitrobenzalmethylsemicarbazone*, m. p. 207—208°; *m-nitrophenylmethylhydroxytriazole*, m. p. 285—285·5°; *silver* derivative, $C_9H_7O_3N_4Ag$; *benzoyl-4-methylthiosemicarbazide*, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}N{:}C(SH){\cdot}NHCH_3$, m. p. 198°; 2-*phenyl*-1-*methyltriazole*,—

m. p. 112—113°; 2-*phenyl*-1-*methylmercaptotriazole*, m. p. 163—164°. Methylsemicarbazide, formed by the action of potassium cyanate on methylhydrazine sulphate, has the methyl group in position (2), $NH_2{\cdot}N(CH_3){\cdot}CO{\cdot}NH_2$, and not in position (1), $CH_3NH{\cdot}NH{\cdot}CO{\cdot}NH_2$ (compare Brüning, *Ann.*, 1889, cclxiii., 11).

Discussion.

Dr. Silberrad pointed out that Knorr's theory affords a better explanation than that given by the author of facts such as that illustrated by the identity of the triazoles represented by the formulæ—

a phenomenon to which attention was drawn on the conversion of dihydrotetrazine into the triazole represented above (Hantsch and Silberrad, *Ber.*, 1900, xxxiii., 89).

In reply, Dr. Young said that the identity of Freund's triazole with that prepared from tetrazine was in agreement with the view put forward in the paper as to the "amidine" nature of the triazole ring.

59. "*Researches on Moorland Waters.* Part II. *On the Origin of the Combined Chlorine.*" By W. Ackroyd.

The object of the investigation has been to discover the origin of the common salt in the water of the Widdop reservoir in Yorkshire, about midway between the two seas, this water being continually removed, and as continually replenished from the saltless area of Millstone Grit and Yoredale rocks. The chlorine in the winter rainfall more than accounts for it, and the conclusions arrived at are (1) that the combined chlorine in the reservoir water is wholly derived from rain water; (2) that the quantity of chlorine in the reservoir, whose capacity is 640½ million gallons, closely approximates to a yearly average of 1·188 parts per 100,000, and (3) that in winter the chlorine in the rainfall is in excess of the average for other seasons of the year.

60. "*Robinin, Violaquercitrin, and Osyritrin.*" By A. G. Perkin.

Robinin, isolated from the flowers of *Robinia pseudacacia* by Zwenger and Dronke (*Ann. Sup. I.*, 1861, 257), was considered by them as a glucoside of quercetin. The formula $C_{33}H_{38}O_{20},8H_2O$ is now assigned to the air-dried substance, and its decomposition with dilute mineral acids may be thus represented,—

$$C_{33}H_{38}O_{20}+4H_2O=C_{15}H_{10}O_6+3C_6H_{12}O_6.$$

The *colouring matter*, $C_{15}H_{10}O_6$, melts at 271—272°, yields a *sulphate*, $C_{15}H_{10}O_6,H_2SO_4$, and a *tetracetyl* derivative, $C_{15}H_6O_6(C_2H_3O)_4$. On decomposition with alkali, phloroglucinol and *p*-hydroxybenzoic acid are formed. It is identical with *kampherol*, which is present as its monomethyl ether, kampheride, in galanga root (*Alpinia officinarum*) (Gordin, *Dissert.*, Berne), and as glucoside in *Delphinium consolida* (*Proc.*, 1900, xvi., 182). The sugar gave a mixed osazone, from which dextrosazone (m. p. 204—205°), and a more soluble compound, m. p. 190—196° (possibly the galactose derivative), were isolated.

Osyritrin, the quercetin glucoside of *Osyris compressa* (*Trans.*, 1897, lxxi., 1131), has at 130° the formula $2C_{27}H_{28}O_{16},H_2O$, and not $C_{27}H_{30}O_{17}$, as previously stated. Air dried, it contains $3H_2O$, and is anhydrous at 160°. Violaquercitrin (Mandelin, *Jahres.*, 1883, 1369), present in the *Viola tricolor*, has at 160° the formula $C_{27}H_{28}O_{16}$, and not $C_{42}H_{42}O_{24}(=C_{27}H_{26}O_{15})$ there given. Air dried, it contains $3H_2O$, and is identical with osyritrin.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, April 26th, 1901.

Dr. R. T. Glazebrook, Foreign Secretary, in the Chair.

A paper on "*The Thermodynamical Correction of the Gas Thermometer*" was read by Prof. H. L. Callendar.

This paper commences by giving a short historical sketch of the thermodynamic correction of the gas thermometer, describing some of the solutions to Thomson's fundamental equation for the Joule-Thomson plug experiment. The assumptions made in the solutions have sometimes been erroneous, and wrong corrections have been obtained. From 1885 to 1888 Chappuis made a series of careful comparisons between various gas thermometers and a very delicate mercury thermometer, and drew up a table of differences between the hydrogen and the nitrogen thermometer. The author has taken the observations of Chappuis, and calculated a new table of differences. The index "n" in the modified Joule-Thomson equation is not constant. For steam it is about 3·5, and for carbonic acid about 2. The thermodynamic correction is very small, especially in the case of hydrogen and helium, and is very much less than the correction for the expansion of the thermometer bulb.

Prof. Herschell asked whether the co-volume came into the correction.

Dr. Harker looked forward to the experiments which Prof. Callendar proposes to make with a constant pressure thermometer.

The Chairman expressed his interest in the extreme delicacy of the observations of Chappuis.

A paper on "*The Production of a Bright Line Spectrum by Anomalous Dispersion and its Application, the 'Flash Spectrum,*'" by R. W. Wood, was read and experimentally illustrated by Mr. Watson.

It has been suggested by W. H. Julius that the "flash spectrum" seen immediately at totality may be due to photosphere light abnormally refracted in the atmosphere of metallic vapours surrounding the sun. The light which will be thus abnormally refracted will be of wave-lengths almost identical with the wave-lengths which the metallic vapours are themselves capable of radiating. The sun is supposed to be surrounded by an atmosphere of metallic vapours, the refractive index of which decreases with increasing distance from the surface. In this atmosphere the rays of light coming from the photosphere move in curved paths. The refractive index is, however, very small except for wave-lengths very near those absorbed by the vapour. Consequently, the light which resembles that emitted by the vapours is most strongly refracted, and therefore curves sufficiently to reach us after the photosphere has been hidden by the moon. The flash spectrum of sodium was shown by focussing the light of an arc lamp on a horozontal slit in front of a flat metal plate supported so that the plane in which its under surface lay coincided with the plane of the slit. At a distance of about two metres a direct vision spectroscope was arranged to give a vertical spectrum, and placed at such a height that the prism barely caught the rays coming from the slit and grazing the plate. On looking into the spectrosocope a bright continuous spectrum is seen. A Bunsen burner was then placed underneath the metal plate, and fed with sodium. This produced a layer of sodium vapour of varying refractive index. On raising or lowering the spectroscope sodium lines are seen due to anomalous dispersion. By arranging screens these lines can be obtained so that on cutting out the arc lamp the flash spectrum vanishes.

Prof. Herschell expressed his interest in the experiments, and their application to the case of the flash spectrum seen at totality.

The Society then adjourned until May 10th, 1901.

NOTICES OF BOOKS.

Researches on Leadless Glazes. By William J. Furnival. Stone, Staffordshire: W. J. Furnival. Pp. 135.

The value and importance of a satisfactory leadless glaze for pottery can hardly be over-estimated, not so much from the point of view of durability, though this must not be forgotten, but from the fact that there is a very large amount of unnecessary suffering and injury to health, often followed by early death, caused by the use of carbonates and oxides of lead as ingredients of the fluxes from which the glazes are formed.

It has been claimed that the fritting of the lead compounds with siliceous materials renders lead glazes less injurious, but even in this state danger still exists. If, it is asked, fritted lead compounds are to be used for glazes, how are they to be obtained? Who is to frit them, and how are they, who do the fritting, to be protected? These questions can be best disposed of by doing away with lead glazes altogether.

The problem is no doubt a difficult one, but, as the author says, "to fold our hands and say it cannot be solved, finality has been reached, discoveries are at an end; or to be content simply to prepare a defence for the continued use of lead in glazes, is both impolitic and unprogressive."

It is a fact that durable glazes free from lead have been and are now being used for hard porcelain, and to some extent for stoneware and bricks, and the recipes for a number of such glazes will be found in these pages.

The *durability* of leadless glazes has been greatly contested, but the author brings forward a number of historical examples which prove beyond question the exact opposite; he is, however, content to abide by the statement that the durability of a leadless glaze is not necessarily less than that of a lead glaze.

The chapter on "Special Research Experiments" is both of importance and interest, and though many of the experiments were associated with failure they all have their value; it is not unfrequent that more is learnt from a so-called unsuccessful experiment than from a successful one. This chapter is followed by one on "Practical Recipes," of which a considerable number are given.

Opalinity and opaline tendencies have probably been the most troublesome defects experts have had to overcome in the preparation of satisfactory leadless glazes; experience seems to point to lime, potash, zinc, and silica as the chief offenders, though some experiments show that calcium compounds are not always in fault. Blistering has been another cause of trouble, though it may be remarked that this will also occur with some lead glazes. A very important matter is regularity in mixing, and probably few things are more essential than good firing.

The book is well printed, serviceably bound, and furnished with a good index. The author has written as a practical man, and his knowledge and experience of the subject should be of great assistance to all those, and they must be many, who are interested in leadless glazes.

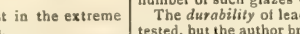
CORRESPONDENCE.

TAUTOMERISM.

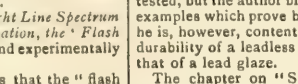
To the Editor of the Chemical News.

Sir,—There is a remarkable point about tautomerism that I have not seen mentioned before, and which is certainly worth recording, viz., that the mobile hydrogen atom always travels from a position which we may call (1) into the position (3).

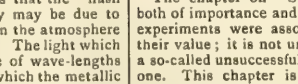
Examples.



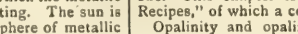
Cyanic acid.



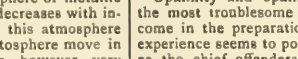
Guanin.



Isatin.

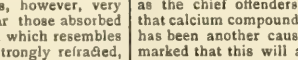


Diazobenzene.

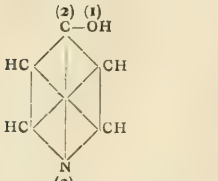


Ethylaceto-acetate.

The following two examples require the adoption of particular formulæ which have been put forward.



Azobenzene phenol.



γ-Pyridone.

If this rule be correct it will favour the peroxide formulation for quinones, &c., and the γ bond in the pyridine series (when γ substituents).—I am, &c.,

A. Lionel Landau.

20, Highbury New Park,
April 22, 1901.

RAPID ESTIMATION OF PHOSPHORUS IN STEEL.

To the Editor of the Chemical News.

Sir,—In reply to a correspondent, referring to my communication on the "Rapid Estimation of Phosphorus in Steel" (Chem. News, vol. lxxxiii., p. 154), the letter "E" stands for "Equivalent," and an E solution is one containing a gramme equivalent of reacting substance per litre, or a milligramme equivalent in 1 c.c. For example—

16 E HNO_3 contains 16 grms. equivalents HNO_3 per litre.
10 E HCl „ 10 „ „ HCl „

Your correspondent will find a description of the "Equivalent System" in an article by J. Reddrop, F.I.C., which appeared in the Chemical News, May 23, 1890 (vol. lxi., p. 245), also in Morgan's "Tables for Quantitative Metallurgical Analysis."—I am, &c.,

J. Jas. Morgan.

Wednesbury, April 25, 1901.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxii., No. 14, April 9, 1901.

Generalisation of Trouton's Law.—M. de Forcrand.—In 1844 Trouton enunciated the law bearing his name. This law establishes an empirical relation between latent heats of vaporisation, measured at the normal temperature of ebullition, and this temperature reckoned from absolute zero, $\frac{L}{T} = K$; K varying from 20 to 26. The author investigates this law, and finds that it can be stated more generally as follows:—In all chemical or physical phenomena, the heat of solidification of any gas whatsoever is proportional to its temperature of vaporisation under atmospheric pressure, $\frac{L+S}{T} = 32{\cdot}1$. The constant varies very slightly for the substances on which the experiments were made, viz., ammonia, water, glycol, chlorine, bromine, iodine, phenol, benzene, naphthalene, ethylene bibromide, methyloxalate, butyric, formic, and acetic acids. The mean value of the constant from all the experiments being 30.

New Method of Distinguishing Colouring-matters. Application to Indophenols.—C. Camichel and P. Bayrac.—The authors' experiments prove—(1) That when a tertiary nitrogen is replaced by a primary nitrogen, the minimum of transparence is displaced towards the most refrangible end of the spectrum, whatever be the solvent (alcohol, ether, carbon disulphide, or chloroform); (2) an ortho-substitution in the phenol from which indophenol is derived produces a considerable displacement of the minimum of transparence, whatever be the solvent; (3) a meta-substitution in the same phenol produces a very slight displacement of the transparence minimum towards the red or towards the blue. This displacement is often zero, and it differs little from experimental errors.

Reaction of Amido-substituted Benzophenones and the Aromatic Amines in Sulphuric Medium.—Paul Lemoult.—In a sulphuric medium, the para-amido-substituted benzophenones give, with certain aromatic amines, but not with others, reaction products which are colouring-matters. The only amines which are capable of this reaction are those which have at least two aromatic radicles joined directly to the nitrogen. It is also necessary that one of these radicles be a phenyl, and that it have the free para-position (nitrogen being in 1); in this case the splitting of the two molecules takes place at that point.

MEETINGS FOR THE WEEK.

Monday, 6th.—Society of Arts, 8. (Cantor Lectures). "Alloys," by Sir William Chandler Roberts-Austen, K.C.B., F.R.S.

—— Society of Chemical Industry, 8. "Action of Caustic Potash and Soda on Stannous Sulphide," by Dr. F. Mollwo Perkin. "The Relative Leather-forming Value of the Different Tanning Materials—their Speed of Tanning, with Notes on the Quality," by John Youl and R. W. Griffith. "The Need of Greater Care in introducing Gas-Firing into Small Gas-works," by W. Cecil Jones. "Arsenic in Coal and Coke," by R. F. Wood Smith and R. L. Jenks.

Tuesday, 7th.—Royal Institution, 3. "On Cellular Physiology, with special reference to Enzymes and Ferments," by Allan Macfadyen, M.D., B.Sc.

—— Society of Arts, 4.30. "The Coal Problem—its Relations to the Empire," by Lieut. Carlyon W. Bellairs, R.N.

Wednesday, 8th.—Society of Arts, 8. "School Work in relation to Business," by Sir Joshua Fitch, LL.D.

Thursday, 9th.—Royal Institution, 3. "Arthur Sullivan" (with Vocal and Instrumental Illustrations), by Sir Alex. Campbell Mackenzie, Mus.Doc.

Friday, 10th.—Royal Institution, 9. "The Response of Inorganic Matter to Mechanical and Electrical Stimulus," by Professor Jagadis Chunder Bose, M.A., D.Sc.

—— Society of Arts, 8. (Howard Lectures). "Polyphase Electric Working," by Alfred C. Eborall, M.I.E.E.

—— Physical, 5. "Applications of Elastic Solids to Metrology," by Dr. C. Chree, F.R.S. "The Thermal Properties of Isopentane compared with those of Normal Pentane," by Prof. S. Young, F.R.S., and J. Rose-Innes.

Saturday, 11th.—Royal Institution, 3. "The Rise of Civilisation in Egypt," by Prof. W. M. Flinders Petrie, D.C.L.

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THE CHEMICAL NEWS.

Vol. LXXXIII., No. 2163.

THE USE OF METALLIC SODIUM IN BLOWPIPE ANALYSIS.

By CHARLES LATHROP PARSONS.

The use of sodium carbonate to assist the action of the reducing flame has long been customary in blowpipe analysis, and is adopted by all text-books on the subject. The reducing action is partly due to the formation of sodium cyanide, but more largely to the formation of gaseous sodium and carbon monoxide. At best its action is slow, and nothing more severely tests the skill of the beginner than the attempt to obtain a button of metallic tin from cassiterite, or the sulphur reaction from gypsum. In general it is much more difficult to reduce an oxide or sulphide before the blowpipe, than it is to cause the opposite reaction to take place by means of the oxidising flame. Therefore, if the assay is not kept in the reducing zone of the flame, a re-oxidation will almost certainly take place.

The great reducing power of powdered aluminum has been well illustrated by Goldschmidt and Vautin (*Journ. Soc. Chem. Ind.*, xvii., 545), and, although the fact that this property is possessed also by magnesium and sodium has long been known, W. Hempel (*Zeit. Anorg. Chem.*, xvi., 22), seems to have been the first to propose the use of the latter as a reagent in qualitative analysis. Hempel calls attention to the ease with which reduction may be brought about by sodium, but states that it does not give satisfactory results on charcoal. He recommends that the sodium be flattened out upon an ordinary filter-paper, and after being mixed with the powdered substance, folded once and then rolled so that a double layer of paper is between each layer of sodium. This roll is next enclosed in a spiral of iron wire, set on fire in a Bunsen flame, and cooled in the unburned gas below. It is next triturated with water in an agate mortar, and the residue carefully examined.

I have found these details to be quite unnecessary, and that the reaction takes place with the greatest ease upon charcoal. To the operator who has been used to the much more tedious reduction with sodium carbonate the quickness and certainty of the results are almost startling, and the reduction takes place with silicates, chlorides, carbonates, borates, sulphates, sulphides, &c., with as much ease and accuracy as with the oxides themselves. The method is extremely simple.

A small piece of metallic sodium, not more than 3 or 4 m.m. in diameter, is hammered out flat on some smooth surface. The substance to be reduced is powdered and spread upon it, pressed into the metal with the hammer, and the whole turned and kneaded into a little ball with a knife-blade. It is then placed upon a slight depression in a piece of charcoal, and ignited with a match or the Bunsen flame. A momentary flash ensues, and the reduction is accomplished. The residue is now heated before the blowpipe, and as the sodium oxide and hydroxide immediately sink into the charcoal, any fusible metallic particles collect easily into a button, and may be recognised in the usual manner. Volatile metals, like zinc, oxidise and yield with surprising readiness their characteristic coatings, and on digging up a little of the charcoal, moistening with water, and placing upon a silver coin, the "Hepar" reaction is obtained if sulphur was present in any form. It is perhaps superfluous to add that this last reaction is certain in its conclusions only when carried out upon a piece of charcoal uncontaminated by previous tests.

Applied to minerals the method yields results but little less certain than when pure salts or oxides are reduced. Galenite yields at once a button of lead which in the oxidising flame gives the lead coating without a trace of the white coating of sulphate which ordinarily results. Garnierite gives a residue of silicon and magnetic nickel to which the bead test can be immediately applied. Chrysocolla and cassiterite yield buttons of copper and tin respectively as readily as a button of lead is obtained from cerusite. Even chromite is immediately reduced, and if the residue is powdered the iron may be quite largely separated from the chromium by means of the magnet. Barite, celestite, and gypsum show with ease the sulphur reaction, and the residue if moistened with hydrochloric acid gives the flame tests far more rapidly than if applied to the powdered minerals. In general the method is applicable whenever reduction can take place, and whenever the reduced material yields characteristic reactions more readily than the mineral itself.

The metallic sodium does not need to be kept under naphtha, but may be supplied to a class in small rubber-stoppered wide-mouthed bottles. A lump of sodium two or three centimetres in diameter will keep for months in this manner with only superficial oxidation. It must, of course, be carefully kept away from water or moisture. In rolling up the sodium and substance to be reduced into a ball, the metal should not be touched with the fingers, for with one or two of the more easily reduced oxides or sulphides, the reaction sometimes begins spontaneously. This takes place quite readily with the peroxide of lead. Large quantities of sodium should be avoided or the reaction may become dangerously violent.

From my experience in its use with classes during the last two years, I feel sure that sodium will soon be universally employed as a reagent in blowpipe laboratories. —*Journal of the American Chemical Society*, vol. xxiii., No. 3.

THE ESTIMATION OF SULPHYDRIC ACID IN COAL-GAS.

By A. MULLER.

I have had occasion to use the following method for the estimation of sulphuretted hydrogen in coal-gas (*Stahl und Eisen*, 1896, p. 865). This process being simple, exact, and rapid, I thought it would be of interest to describe it, as it can be employed with great advantage in the laboratories of large gas-works.

Two solutions are required:—

1. *Solution of Acetate of Cadmium.*—Twenty-five grms. of acetate of cadmium and 200 c.c. of acetic acid are made up to 1 litre with distilled water.
2. *Solution of Sulphate of Copper.*—Eighty grms. of powdered crystals of sulphate of copper in 750 c.c. of distilled water. After cooling, 175 c.c. of concentrated sulphuric acid are added, and the whole made up to a litre; if necessary, the solution is filtered.

Twenty-five c.c. of No. 1 solution are placed in an Erlenmeyer flask fitted with a cork pierced with two holes. Two glass tubes pass through these holes: one, for the entry of the gas, reaches to the bottom of the flask; the other opens directly to the air.

The volume of gas which passes through the solution is measured accurately. A carboy of about 15 litres capacity could be used, and the gas driven from it by means of a known volume of water; the whole must be arranged so that the current of gas is not too rapid. There need be no fear that the whole of the sulphuretted hydrogen will not be absorbed; this can easily be guarded against, however, by having two absorption flasks in series, instead of one only.

The operation terminated, the cork with the glass tubes

is removed, and the contents of the flask are heated to 50—60°, and 10 c.c. of the solution of sulphate of copper are added. The sulphide of cadmium and the sulphate of copper immediately react, and the precipitate, which is first yellow becomes black. It is then filtered, washed with warm water, dried, calcined, and weighed. The reactions which take place are the following:—

$$H_2S+Cd(C_2H_3O_2)_2=CdS+2C_2H_4O_2,$$
$$CdS+CuSO_4=CdSO_4+CuS,$$
$$CuS+3O=CuO+SO_2,$$

One molecule of sulphydric acid thus corresponds to one molecule of oxide of copper, and we get the proportion—

$$CuO : H_2S :: 79 : 34.$$

Under normal conditions, the weight of 1 litre of sulphuretted hydrogen is 1·5232 grms.

We may take it, as a rule, that the temperature at which the analyses are made is 18°. At this temperature 1 litre of gas weighs 1·43 grms. We arrive at the number of litres of sulphuretted hydrogen contained in the quantity of coal-gas analysed, by multiplying the weight in grms. of the oxide of copper found by $\frac{34}{79 \times 1{\cdot}43} = 0{\cdot}301$.—

Journ. für Gasbeluchtung und Wasserversorgung, xliii.

SOME PRINCIPLES AND METHODS OF ROCK ANALYSIS.*

By W. F. HILLEBRAND.

(Continued from p. 213).

XIX. *Ferrous Iron.*

Comparison of Sealed-tube and Hydrofluoric Acid Methods —Comparative Worthlessness of the Former in Rock Analysis.

No point in rock analysis has been the cause of greater solicitude to the chemist, and especially to the mineralogist and petrographer, than the determination of iron in ferrous condition. The sealed-tube or Mitscherlich method with sulphuric acid, for a long time the only available one, is in theory perfect, since complete exclusion of oxygen is easily attainable. Its chief hitherto recognised defect lies in the inability to always secure complete decomposition of the iron-bearing minerals, and even to ascertain, oftentimes, whether or not the decomposition has been complete. The addition of hydrofluoric acid to the sulphuric in the tube, in order to insure this breaking up, is to be regarded as of very doubtful utility in most cases, since the glass may be so strongly attacked as to add an appreciable amount of iron to the solution, and the hydrofluoric acid may have exhausted itself in attacking the glass before the more refractory minerals succumb. Nevertheless, if decomposition can be effected by sulphuric acid alone the results obtained are sharp and concordant, and what has seemed especially remarkable, and up to almost the present moment without a satisfactory explanation, they are in rock analysis usually higher than when made by any of the modifications of the hydrofluoric acid method now so extensively practised. This difference is not very marked with rocks containing but 1 or 2 per cent of ferrous iron, but it increases with rising percentages to such an extent that where the sealed-tube method will show 12 per cent FeO the other may indicate no more than 10 per cent. This is a fact of which the writer has long been cognisant, but it does not seem to be known to chemists or petrographers at large, though Wülfing (*Ber. Deutsch. Chem. Gesell*, 1899, vol. xxxii., p. 2217, footnote), has noticed this difference in certain analyses without appreciating its significance. Experiments with soluble iron salts of known composition, like ferrous sulphate and ferrous-ammonium sulphate, throw no light on the subject, for both methods give with them the same sharp and accurate results.

In spite of several attempts to find a solution to the problem, none presented itself until very recently, when, as a result of observations made in this laboratory by Dr. H. N. Stokes in a pending investigation on the action of ferric salts on pyrite and other sulphides, the clue was given. Dr. Stokes found that ferric salts exercise a most marked oxidising effect on pyrite and probably other sulphides. The reaction is not new (see J. H. L. Vogt in *Zeit. fur Prakt. Geol.*, 1899, pp. 250—251), but the ease with which the change takes place, and the completeness of the oxidation of the pyrite, not only of its iron but of the greater part of the sulphur as well, were entirely unexpected. Pure pyrite itself is attacked with extreme slowness by boiling dilute sulphuric and hydrofluoric acids, either alone or mixed, but the moment a ferric salt is introduced the case is altogether different.

However, experiment has shown (see *prox.*), that with the amounts of sulphides usually found in igneous rocks their effect upon the estimation of ferrous iron by the hydrofluoric acid method at atmospheric pressure and boiling heat is negligible, though by increasing the amount of sulphide the effect becomes more and more apparent, because of the greater surface of pyrite exposed to the action of the ferric iron of the rock.

Under the conditions of the Mitscherlich method, on the other hand—a temperature of 150 to 200° C., and even higher, high pressure, much longer time of action, and im possibility of escape of any hydrogen sulphide that may be formed—the sulphur of the sulphides becomes nearly, if not fully oxidised to sulphur acid at the expense of the ferric iron in the rock, with the production of an equivalent amount of ferrous iron in addition to that resulting from the sulphide itself. Now, rocks with hardly an exception, and many minerals, carry pyrite or pyrrhotite, or both, often in considerable amount, often in traces only. My own experience has been that sulphur can almost always be detected in 2 grms. of rock powder.

Let us now see what the effect of these traces when fully oxidised amounts to. One atom of sulphur (32) requires for its complete conversion to trioxide the oxygen of three molecules of ferric oxide (480), which then becomes six molecules of ferrous oxide (432). In other words, 0·01 per cent of sulphur may cause the ferrous oxide to appear too high by 0·135 per cent, and 0·10 per cent of sulphur may bring about an error of 1·35 per cent in ferrous oxide. The case is still worse if the sulphur is set free as hydrogen sulphide from a soluble sulphide, for then the above percentages of sulphur produce errors of 0·18 and 1·8 per cent respectively, in the ferrous oxide determination.

The error caused by sulphides tends to become greater the more there is present of either or both sulphide and ferric salt. Now, the highly ferruginous rocks usually carry more ferric iron than the less ferruginous ones, and they are often relatively high in pyrite and pyrrhotite; hence the increasing discrepancy between the results by the two methods as the iron contents of the rocks rise is fully in accord with the above explanation.*

Notwithstanding that the Mitscherlich method has thus been discredited in its general applicability to rocks and minerals, it is still capable of affording valuable assistance with those which are totally free from sulphides. Hence the conditions under which success can best be achieved by it are set forth in the following paragraphs.

The Modified Mitscherlich Method.

Strength of Acid.—The method in its original and usual application calls for a mixture of three parts of sulphuric

* *Bulletin of the United States Geological Survey*, No. 176.

* For details of experiments showing the worthlessness of the Mitscherlich method for rocks and minerals which contain even a trace of free sulphur or sulphides see Hillebrand and Stokes, in an as yet unpublished paper in *Journ. Am. Chem. Journ.*, vol. xxii., and *Zeit. fur Anorg. Chem.*, 1900, vol. xxv., entitled "Relative Value of the Mitscherlich and Hydrofluoric Acid Methods for Ferrous Iron Determinations."

acid and one of water by weight, or about three to two by volume, though a still stronger acid is sometimes used. In some cases, however, perhaps in most, much better decomposition of the silicates is effected by reversing the proportions of water and acid, or at any rate by diluting considerably beyond the above proportion. Hereby the separation of salts difficultly soluble in the stronger acid is avoided, and the actual solvent effect on the minerals seems to be in no wise diminished.

Filling, Sealing, and Heating of the Tube.—The very finely powdered mineral having been introduced into a tube of resistant glass free from ferrous iron, the open end is drawn out, so as to leave a funnel for the introduction of the acid. A very little water is then introduced, and carefully heated to boiling for a moment to expel all air from the powder. The diluted acid—which has just been boiled down from a state of greater dilution in order to have it free from air—is then poured in until the tube is about three-fourths filled. Carbon dioxide is then introduced from a generator which has been in active operation for some time, through a narrow glass tube drawn out of the same kind of glass as that of which the decomposing tube consists. In a few moments the air is expelled, and the small tube is then sealed into the large one over the blast-lamp without interrupting the gas current until the very last instant, when to prolong it would perhaps cause a blowing out of the softened glass. The interruption of the current at the proper moment is easily effected by the pressure of the thumb and finger holding the small tube at the point where it enters the rubber tube leading from the gas generator. No breakage in the oven ever occurs as a consequence of thus fusing one tube into the other.

The heating is done in a bomb oven at any desired temperature up to, say, 200° C., and continued at intervals until examination by aid of a low-power lens shows that decomposition is complete or has progressed as far as can be hoped for. By enclosing the glass in an outer tube of strong steel, properly capped (Ullmann, *Zeit. fur Angew. Chemie*, 1893, p. 274; *Zeit. fur Anal. Chemie*, 1894, vol., xxxiii., p. 582), and containing a little ether or benzene to equalise the pressure on both sides of the glass, the temperature can be elevated far beyond what is otherwise permissible, and the decomposition will then doubtless be more complete with refractory silicates.

Reason for Introducing Gas and Sealing as above Directed.—The usual practice in employing the above method has been to expel air before sealing by introducing a few crystals or lumps of an alkali carbonate or bicarbonate, the gas set free on their contact with the acid being supposed to effectively expel all air. That this is not accomplished the following series of comparative results long since published elsewhere (*Bull. U.S. Geol. Survey*, No. 78, p. 50; CHEMICAL NEWS, 1891, vol. lxiv., p. 232) fully show. The material used was the oxide of uranium, U_3O_8, requiring by theory 32·07 per cent of UO_2. Operating as just above described on from 0·3 to 0·5 grm., the results were—

31·06, 31·07, 29·72, 29·33, 29·89, 30·69,

whereas after filling the tube with gas from a generator there was found—

32·11, 31·90, 32·15, 32·12, 32·06, 32·17, 32·28.

the average error of the former series being 1·78 per cent. The percentage error would, of course, be reduced by increasing the weight of mineral operated on. An average error equal to the above when employing 1 grm. of ferrous minerals would make the percentage for FeO about 0·3 per cent too low. While the absolute error might be the same in all cases, the relative error would increase with minerals low in ferrous iron.

The Hydrofluoric Acid Method.

This method is the one which has been almost exclusively used since the earliest years of the Survey's existence.

This specially ground powder, in a capacious crucible, is placed, after stirring up with dilute sulphuric acid, on a small water-bath of a single opening (Fig. 13), and covered with a glass funnel, the stem of which has been cut off near the flare, resting in a depression of the specially made cover, into which water constantly drops from a tubulated bottle, thus securing a perfect water joint, and serving to keep the bath full. Through a small metal pipe carbonic-acid gas flows into the bath above the surface of the water, and rising through orifices in the cover fills the funnel and crucible (J. P. Cooke, *Amer. Journ Sci.*, 1867, Second Series, vol. xliv., p. 347). The lamp under the bath is lighted, and hydrofluoric acid is poured into the crucible through a platinum funnel, which is left in place to serve as an occasional stirrer, for which a rod or wire may be substituted. After boiling commences the rapid gas current can be safely interrupted, to be restored when the lamp is extinguished after one-half to one or more hours. A full stream of cold water is then caused to flow from the tubulated bottle into the bath, the overflow from the outlet tube being caught in a receiver. As soon as cool the contents of the crucible are emptied into a platinum

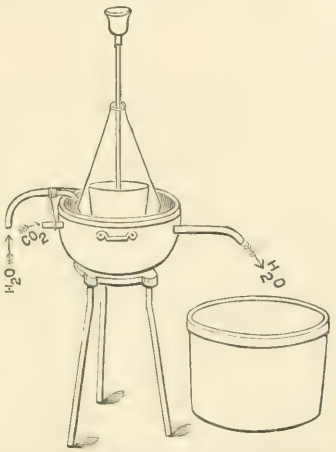


FIG. 13.—COOKE'S APPARATUS FOR THE DETERMINATION OF FERROUS IRON.

dish containing cold water, and titrated till the first permanent colour appears, which usually will last for only a few seconds. Duplicate determinations are to be advised whenever possible, since even with the utmost care the results will occasionally differ more than is allowable.

In absence of a suitable water-bath an ordinary one can be used covered with a beaker, through a hole in the bottom of which a strong current of carbon dioxide is introduced, or the crucible may be set in a sand-bath, and covered in the same way with a broken beaker (Doelter).

The cause of the rapid disappearance of the first pink blush when titrating in hydrofluoric-sulphuric solution appears to be the ready oxidisability of manganous fluoride by permanganate. The latter can be added by the cubic centimetre to solutions already containing manganous sulphate in presence of hydrofluoric acid without producing a more than passing pink blush. The solution, however, takes on in ever-increasing intensity the red-brown colour characteristic of manganic salts. The decolorisation due to this cause is hence much more pronounced in the case of rocks high in ferrous iron than of those low in this

constituent, because of the greater amount of manganous salt resulting from reduction of a correspondingly larger amount of permanganate.

When pyrite is present the bleaching is in part due to its action on any permanganate added in excess of the requirements of the ferrous oxide. But this action is not so immediate as to affect the ferrous oxide determination if the end point in the latter has been properly observed.

Pratt's Modification of the Hydrofluoric Acid Method.

J. H. Pratt (*Amer. Journ. Sci.*, 1894, Third Series, vol. xlviii., p. 149), has shown that very satisfactory ferrous iron determinations can be secured by simple boiling of the rock powder with hydrofluoric and sulphuric acids in a large crucible fitted with a cover and platinum tube for introduction of carbon dioxide. His test experiments on ferrous sulphate show that there need be practically no oxidation, even if the heating lasts several hours. The directions given on page 150 of his paper, with reference to the treatment of very refractory minerals which are not fully decomposed by this treatment, must be understood as referring only to homogeneous minerals, and not to rocks, where the relations of ferrous and ferric iron in the undecomposed portion are certainly different from those in the part dissolved.

Influence of Sulphides, Vanadium, and Carbonaceous Matter on the Determination of Ferrous Iron by the Hydrofluoric Acid Method.

A dark colour of the undissolved residue may be due to pyrite, graphite, or carbonaceous matter. The first of these affects the result but little, the second probably not at all, and they can be distinguished by their behaviour toward nitric acid. Organic matter of course renders impossible the estimation of ferrous iron.

Sulphides.—Pyrite in the quantities usually met with in igneous rocks, is probably without serious effect on the ferrous-iron determination by any of the hydrofluoric acid methods. This sulphide is very resistant toward attack in the absence of oxygen, as is shown by the fact that if present in any quantity it can be readily recognised in the residue after titration. In any case it is impossible to allow for an error introduced by its possible decomposition, and the result of titration must count as ferrous iron. In the case of soluble sulphides two sources of error are introduced—that of reduction of ferric iron by hydrogen sulphide evolved, and that due to the ferrous iron which the sulphides themselves may contain, especially if pyrrhotite is present. The first of these is perhaps negligible, since most of the hydrogen sulphide would probably be expelled without reducing iron. The second is approximately measurable if it is known that pyrrhotite is the only soluble sulphide present, and its amount has been ascertained by determining the hydrogen sulphide set free on boiling with hydrochloric acid in a current of carbon dioxide. In this case a correction is to be applied to the result of titration for total ferrous iron. See also *prox.*, under "Sulphur."

In order to obtain quantitative data regarding the effect of pyrite on the ferrous-iron estimation by the hydrofluoric acid method the following tests were recently made:—Part of a fine crystal of pyrite was rather finely powdered and boiled with dilute sulphuric acid, which extracted considerable ferrous iron, derived presumably from admixed or intergrown pyrrhotite, since a second boiling with fresh acid gave a negative test for ferrous iron. After washing by decantation with water, followed by alcohol and ether, the powder was dried and further pulverised. A quarter of a grm. of it when treated with hydrofluoric and sulphuric acids in a large crucible by the Cooke method for ferrous iron, then rapidly filtered through a very large perforated platinum cone fitted with filter-paper, required but 2 drops of a permanganate solution representing only 0·0032 grm. FeO to the c.c.

Since, however, Dr. H. N. Stokes has found in a pending investigation that the oxidising effect of ferric salts on pyrite and other sulphides is vastly greater than seems to have been suspected (see p. 218), the following tests were made in order to ascertain the probable error due to this action under the conditions prevailing in rock analysis:—Successive portions of 1 grm. each of a hornblende-schist, free from sulphur, and carrying 10·09 per cent FeO as the mean of several determinations, and 4·00 per cent Fe_2O_3, were mixed in a large (50 c.m.³) platinum crucible with 0·02, 0·025, and 0·10 grm., respectively, of the above purified pyrite powder, and treated with hydrofluoric and sulphuric acids by the Cooke method, the water-bath being at boiling heat for one hour. The cooled contents of the crucible were poured into a platinum dish containing water, and titrated rapidly nearly to an end. Then, in order to get rid of the pyrite, which would obscure the end reaction by its reducing effect on the permanganate, the solution was filtered as above, and in the clear filtrate the titration was carried to completion. The results were 10·02, 10·16, and 10·70. Inasmuch as the smallest of these three charges of pyrite was several times greater than what may be considered an unusually high amount for an igneous rock, it is very evident that for all practical purposes the influence of pyrite on the ferrous estimation by the Cooke method is negligible. At the same time it is to be borne in mind that with increased content in ferric iron an increased amount of pyrite will be attacked, and that the extent of this attack is undoubtedly influenced by the degree of fineness of the pyrite powder.

Vanadium.—If vanadium, when present, exists in the trivalent condition, it necessarily affects with an error varying with its amount the result of titration for ferrous iron. Knowing the amount of vanadium a correction can be applied as follows:—One molecule of V_2O_3 (150·8) in oxidising to V_2O_5 requires as much oxygen as four molecules of FeO (288) when oxidised to Fe_2O_3. The proportion, 150·8 : 288 :: V_2O_3 present : x, therefore gives the figure to be deducted from the uncorrected value for FeO. That this correction is very needful with many of the basic rocks becomes at once evident from the following perhaps extreme example.—

Found 2·50 per cent apparent FeO in a rock containing 0·13 per cent V_2O_3.
Deduct 0·25 per cent FeO equivalent in its action on $KMnO_4$ to 0·13 V_2O_3.
Leaving 2·25 per cent FeO corrected.
Found 5·00 per cent apparent total iron as Fe_2O_3 in the same rock.
Deduct 0·14 per cent Fe_2O_3 corresponding to 0·13 per cent V_2O_3.
Leaving 4·86 per cent corrected total iron as Fe_2O_3.
Deduct 2·50 per cent Fe_2O_3 equivalent to 2·25 per cent FeO.
Leaving 2·36 per cent Fe_2O_3 in the rock.

Failure to correct for the vanadium in both cases would have made the figures for FeO and Fe_2O_3, respectively, 2·50 and 2·22 instead of 2·25 and 2·36 as shown above.

Carbonaceous Matter. — As said before, matter of organic origin other than graphitic carbon renders the results of the ferrous iron determination altogether unreliable.

Uncertainties of the Ferrous Iron Determination.

From the foregoing it is apparent that, despite the utmost care in practical manipulation, the exact estimation of ferrous iron in rocks is one fraught with extraordinary difficulties and uncertainties. Only in absence of decomposable sulphides, and when the amount and condition of vanadium are known, can the result be regarded as above suspicion.

(To be continued).

THE VOLUMETRIC ESTIMATION OF COPPER AS THE OXALATE, WITH SEPARATION FROM CADMIUM, ARSENIC, TIN, AND ZINC.*

By CHARLES A. PETERS.

It is a well-known fact that copper oxalate is insoluble in water and scarcely attacked by moderate amounts of dilute nitric acid (Storer, "Dictionary of Chemical Solubilities," p. 463). Upon this fact Bournemann (*Chem. Zeit.*, xxiii., 565) has recently based a method for the separation of copper from cadmium by precipitating copper as the oxalate in the presence of nitric acid, filtering hot, and estimating the copper, after ignition, by any of the well-known gravimetric methods. Six to 10 grms. of copper, as the oxide, were used for a single determination, and the errors were large. Bournemann does not recommend this process as an accurate analytical method. Classen (*Ber.*, x., *b*, 1316) describes a method for the separation of metals as oxalates by adding to the solution of the salt of the metals a dilute solution of the potassium oxalate (1:6) and concentrated acetic acid to 80 per cent of the total volume. Regarding copper salts in particular, Classen states that precipitation takes place only in dilute solution and then not completely.

It has been the experience of the writer, that the precipitation of copper oxalate from solutions containing at least 0·0128 grm. of the oxide and saturated with the oxalic acid is practically complete. The filtrate in such cases gives no blue colour with ammonia, looking down on a column of liquid in a test-tube, and only a faint brown colour is developed when the filtrate is neutralised, made acid with acetic acid, and tested with potassium ferrocyanide. It is the object of this paper to show that moderate amounts of copper may be determined quantitatively as the oxalate by precipitation with oxalic acid and titration of the precipitate by potassium permanganate, and also to show that moderate amounts of copper may be separated from other metals in the presence of nitric acid by the addition of considerable amounts of oxalic acid.

Before attempting the quantitative separation of copper from solution by the addition of oxalic acid, a few qualitative experiments upon the precipitation of varying amounts of copper sulphate by varying amounts of oxalic acid were tried at different dilutions. In all the experiments the mixtures stood sixteen to twenty hours, and were filtered from two to four times through four filters folded together, and the filtrates were tested both with ammonia and with potassium ferrocyanide. In cases where the filtrate gave no blue colour with ammonia and only a slight precipitate with ferrocyanide, the precipitation was considered practically complete, and the conditions were regarded suitable for the trial of the method quantitatively. In Table I. is recorded the work upon the precipitation of copper sulphate by 0·5 grm., 1·0 grm., and 2·0 grms. of oxalic acid in 50 c.m.³ of solution.

It will be seen readily by comparison of the right

* Contributions from the Kent Laboratory of Yale University. From the *American Journal of Science*, vol. x., No. 59.

TABLE I.

Dilution 50 c.m.³.

	CuO taken as $CuSO_4$. Grm.	Oxalic acid added in solution. Filtrate treated with NH_4OH.	Oxalic acid added in solution. Filtrate treated with $K_4FeC_6N_6$.	Oxalic acid added in crystalline form. Filtrate treated with NH_4OH.	Oxalic acid added in crystalline form. Filtrate treated with $K_4FeC_6N_6$.
2·0 grms. oxalic acid present.	0·018	Blue colour.	Abundant precipitate.	Blue colour.	Abundant precipitate.
	0·031	Trace of blue colour.	" "	Trace of blue colour.	Evident precipitate.
	0·051	—	Evident precipitate.	—	" "
	0·064	—	Trace of precipitate.	—	Trace of precipitate.
1·0 grm. oxalic acid present.	0·018	Blue colour.	Abundant precipitate.	Blue colour.	Abundant precipitate.
	0·031	" "	" "	Trace of blue colour.	Evident precipitate.
	0·051	Trace of blue colour.	" "	—	" "
	0·064	—	Evident precipitate.	—	" "
	0·094	—	Trace of precipitate.	—	Trace of precipitate.
0·5 grm. oxalic acid present.	0·018	Blue colour.	Abundant precipitate.	Blue colour.	Abundant precipitate.
	0·031	" "	" "	Trace of blue colour.	" "
	0·051	Trace of blue colour.	" "	—	Evident precipitate.
	0·064	—	Evident precipitate.	—	Trace of precipitate.
	0·094	—	Trace of precipitate.	—	" "

TABLE II.

CuO taken as $CuSO_4$. Grm.	Oxalic acid added in solution. Grms.	Volume at precipitation. C.m.³.	Filtrate treated with NH_4OH.	Filtrate treated with $K_4FeC_6N_6$.
			A.	
0·031	0·5	50	Blue colour.	Abundant precipitate.
0·031	1·0	50	" "	" "
0·031	2·0	50	Trace of blue colour.	" "
0·031	3·0	50	Slight trace of blue colour.	" "
0·031	3·5	50	—	Evident precipitate.
0·0128	5·0	50	No blue.	Trace of precipitate.
0·0064	5·0	50	Blue colour.	Abundant precipitate.
			B.	
0·0064	0·5	20	Faint blue.	Abundant precipitate.
0·0064	0·5	15	" "	" "
0·0064	0·5	10	" "	Faint precipitate.
0·0064	0·5	5	—	Trace of precipitate.
0·0003	0·5	5*	—	—
0·0003	0·1	1†	—	—

* Precipitate re-dissolved.

† Precipitate remained.

and left hand sides of Table I. that somewhat smaller amounts of copper may be precipitated completely by the addition of crystallised oxalic acid than by the same amount of oxalic acid already in solution. Thus, when dissolved oxalic acid is added to the solution of 50 c.m.³ amounts of copper sulphate less than 0·040—0·050 grm. are not precipitated completely, while under conditions otherwise the same excepting that the oxalic acid is added in crystalline form, the precipitation of amounts as small as 0·030 grm. is practically complete. The amount of oxalic acid in solution necessary for the complete precipitation (after sixteen to twenty hours) of this minimum amount of copper, 0·031 grm. of copper oxide taken as the sulphate, appears, as shown in Table II., A, which follows, to be about 3·5 grms. in 50·0 c.m.³. If the amount of oxalic acid is increased to 5 grms., making the solution saturated for that substance, using the same volume of liquid, the minimum amount completely precipitable is reduced to 0·0128 grm., but not to one-half that amount.

It appears from the experiments of Table II., B, that the volume of liquid in which precipitation takes place influences the complete precipitation of the copper oxalate. Thus the precipitation of 0·0064 grm. of copper oxide taken as the sulphate by 0·5 grm. of oxalic acid is complete in 5 c.m.³ of liquid. The precipitate which falls from 0·0003 grm. of the oxide taken as the sulphate dissolves in 5 c.m.³ of liquid, but remains visible in 1 c.m.³.

As a result of the preliminary experiments, it may be said that the presence of a certain minimum amount of copper, varying with the conditions, is essential to complete precipitation. Thus, at a dilution of 50 c.m.³ a saturated solution of oxalic acid will precipitate with practical completeness copper taken as the sulphate in amounts exceeding the equivalent of 0·0128 grm. of copper oxide; that 2·0 grms. of oxalic acid will precipitate almost completely for the same volume of solution the equivalent of 0·03 grm. of copper oxide; and that 1·0 grm or 0·5 grm. of oxalic acid will precipitate the equivalent of 0·064 grm. of the oxide.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, April 18th, 1901.

Prof. EMERSON REYNOLDS, F.R.S., President, in the Chair.

(Concluded from p. 214).

61. "*Preparation of Orthodimethoxybenzoin, and a New Method of Preparing Salicylaldehyde Methyl Ether.*" By J. C. IRVINE, B.Sc.

The author described a new and rapid method of obtaining salicylaldehyde methyl ether. A mixture of salicylaldehyde and methyl iodide reacts energetically with dry silver oxide, giving a brown oil, from which a 90 per cent yield of the pure product is obtained on distillation. The product (b. p. 236—238°) readily solidifies to a crystalline mass melting at 39—40°. On boiling with potassium cyanide in alcoholic solution, this substance may be condensed to *o*-dimethoxybenzoin, a yellow, crystalline solid melting at 101·5°. A notable reaction of this benzoin is its quantitative conversion into the corresponding methyl ether by the action of silver oxide and methyl iodide. This substance crystallises from ether in prisms melting at 59—60°.

62. "*Action of Hydroxylamine on the Anhydrides of Bromonitrocamphane.*" By M. O. FORSTER.

The compound $C_{10}H_{17}O_2N_2Br$, obtained by the action of hydroxylamine on the anhydrides of 1 : 1-bromonitrocamphane, crystalliises from alcohol in rectangular plates, and melts at 197°; it reduces ferric chloride and ammoniacal silver nitrate. The *hydrochloride, sulphate, picrate, platinichloride,* and the *carbamide* and *benzoyl* derivatives are well-defined. When nitrous acid acts on the substance, the anhydride melting at 240° is regenerated, and potassium permanganate oxidises it to the compound $C_{10}H_{14}O_2NBr$.

The compound $C_{10}H_{16}O_2N_2$, produced by the action of aqueous sodium hydroxide on the foregoing hydroxylamino-derivative, crystallises in rhomboidal plates, and melts at 208°; the *picrate* and *platinichloride* are well-defined.

63. "*On the Estimation of Cocaine and on Di-iodococaine Hydriodide.*" By W. GARSED and J. N. COLLIE, F.R.S.

The object of this research was to find a method for the fairly accurate estimation of cocaine in small quantity.

The estimation of cocaine in presence of cinnamyl cocaine and isatroypl cocaine, and other substances, with which it is associated in coca leaves, has not been attemped, the method only dealing with the estimation of cocaine when free or mixed with benzoyl ecgonine and ecgonine, the products of hydrolysis of pure cocaine. When a solution of cocaine in the form of a salt containing about 1 per cent of cocaine base is titrated by adding excess of decinormal iodine solution till the supernatant liquid contains excess of iodine, a precipitate of di-iodo-cocaine hydriodide, $C_{17}H_{21}NO_4HII_2$, is formed. The excess of iodine in solution can then be estimated by a decinormal sodium thiosulphate solution. The precipitated di-iodo-compound can be collected and weighed, or the cocaine estimated by the amount of iodine used. Any cocaine salt can be used, since the potassium iodide in the solution reacts with the salt, producing the iodide. Di-iodo-cocaine hydriodide is a remarkably stable and crystalline compound, crystallising in large, glistening crystals of constant composition.

Cocaine can be estimated in presence of ecgonine, as ecgonine forms a soluble iodo-compound.

Benzoyl ecgonine, however, interferes to a considerable extent with the estimation of cocaine. Making use of the fact that both benzoyl ecgonine and ecgonine are insoluble in ether or light petroleum, a separation can be effected, as cocaine is soluble in both these solvents. The extracted cocaine can then be weighed directly or titrated with iodine.

64. "*Note on Acetonylacetone.*" By T. GRAY.

The density (0·973) and refractive index (1·4232) of acetonylacetone purified by conversion into the bisulphite compound, $C_6H_{10}O_2,2NaHSO_3+H_2O$, and regeneration therefrom, were determined, and the molecular refraction $\mathfrak{M}_D = 29·85$ found to agree with the value required by the "keto"-formula. Attention was directed to the readiness with which acetonylacetone is resinified by alkalis, by concentrated sulphuric acid, and by gaseous hydrochloric acid.

65. "*Condensation of Acetonylacetone with Hydrazine Hydrate.*" By T. GRAY.

The products of the interaction of acetonylacetone and hydrazine hydrate were described. Condensation in molecular proportions results in the formation of a base, $C_{12}H_{20}N_4$, b. p. 157—158° at 13 m.m., which readily oxidises in air; it forms a hydrochloride, $C_{12}H_{20}N_4,2HCl$, and a chloroplatinate, $C_{12}H_{20}N_4H_2PtCl_6$. The product of the reaction of the ketone with excess of hydrazine hydrate is a white, crystalline substance having the formula $C_{12}H_{24}N_6$, m. p. 130—132°. The substance gradually undergoes decomposition at the ordinary temperature, is a powerful reducing agent, and is readily decomposed by dilute acids with formation of hydrazine salts.

66. "*Preparation of Synthetical Glucosides.*" By H. RYAN, M.A., D.Sc., and W. S. MILLS, M.A.

Acetochlorogalactose was obtained as a faint yellow, semi-solid syrup slowly soluble in cold alcohol, hot

ligroin, ether, and chloroform, scarcely soluble in cold ligroin, by the action of acetyl chloride on well-dried galactose in a dry, cooled, sealed tube. It was extracted with chloroform, washed with iced water and cold sodium carbonate solution; the chloroform solution, dried with calcium chloride and evaporated in a vacuum, left acetochlorogalactose.

By the action of α-naphthol and potassium hydroxide on acetochlorogalactose in alcoholic solution *α-naphthylgalactoside* ($C_6H_{11}O_5{\cdot}O{\cdot}C_{10}H_7$) was obtained as rectangular plates soluble in hot alcohol and hot water, slightly soluble in cold water, insoluble in ether, chloroform, benzene, and ethyl acetate. It reduces Fehling's solution after inversion by hot dilute sulphuric acid. The galactoside does not dissolve in dilute potash, and melts at 202—203°.

m-*Cresylglucoside* was obtained from acetochloroglucose and *m*-cresol in alkaline solution as long, silky, branching needles, scarcely soluble in benzene, chloroform, ethyl acetate, and carbon bisulphide, soluble in cold water and alcohol, readily soluble in hot water and alcohol. It reduces Fehling's solution only after hydrolysis by dilute sulphuric acid, m. p. 167·5—168·5°.

The carvacryl glucoside already prepared from acetochloroglucose was obtained from carvacrol potash and acetobromoglucose prepared by the method of Königs.

67. "*The Influence of Cane Sugar on the Conductivities of Solutions of Potassium Chloride, Hydrogen Chloride, and Potassium Hydroxide; with Evidence of Salt Formation in the last Case.*" By C. J. MARTIN and O. MASSON.

Sugar-solution is generally considered to be a non-electrolyte, but in view of the fact that saccharates exist, it may more probably be viewed as a very slightly ionised acid. To test this point, the conductivities of solutions of hydrogen chloride and of potassium chloride containing varying amounts of sugar were determined, and it was found that the conductivity did not appreciably differ from that of aqueous solutions of these compounds, except in so far as the viscosity of the sugar solution had to be allowed for. On the other hand, when sodium hydroxide was added to sugar solutions of different strengths, it was obvious that the sugar took part in the conduction, and this is attributable to the formation of sodium saccharate, which, like other salts, is largely ionised in dilute solution. The conductivity, even in this last case, was of course influenced by the viscosity of the sugar solution, but even after allowing for this, the proof of ionisation was unmistakable.

68. "*The Aluminium-mercury Couple.* Part III. *Chlorination of Aromatic Hydrocarbons in presence of the Couple. The Constitution of the Dichlorotoluenes.*" By J. B. COHEN and H. D. DAKIN.

The authors have continued their investigation on the action of the aluminium-mercury couple as a halogen carrier in the preparation of the chlorine derivatives of the aromatic hydrocarbons. They have obtained in this way a series of chlorobenzenes from mono- to hexa-chlorobenzene as well as mono-, di-, and tri-chlorotoluenes. Their work, was, however, chiefly devoted to the identification of the dichlorotoluenes formed by this process, a subject which has been under investigation since 1866, with very conflicting results. By careful fractional crystallisation of the following solid derivatives of the mixed dichlorotoluenes, nitro-, dinitro-, sulphonic acids and salts, sulphonic chlorides and amides, and the dichlorobenzoic acids obtained by oxidation, and by a comparison of these with the same derivatives of the six isomeric dichlorotoluenes which they have prepared in a pure state, the authors have now proved that four, namely, (CH_3=1), 1:2:3, 1:2:4, 1:2:6, and 1:3:4, and very probably 1:2:5 dichlorotoluenes are formed in this reaction. The authors propose to investigate the dibromotoluenes in the same manner, as no very satisfactory evidence has been given of the nature of the mixture formed by brominating toluene.

69. "*A Modification of Gutzeit's Test for Arsenic.*" By E. DOWZARD.

An apparatus to free the gas from hydrogen sulphide, &c., by washing was described along with a series of experiments, which show that lead acetate solution only absorbs hydrogen sulphide, whilst a 15 per cent solution of cuprous chloride in hydrochloric acid absorbs hydrogen sulphide, stibine, and phosphine, but has no effect on arsine.

70. "*On the Chemistry of 'Nerium Odorum.'*" By R. C. L. BOSE, M.B.

In his investigations on the poisonous constituents of *Nerium odorum*, the sweet-scented oleander, two methods of analysis of the roots were employed by the author, namely, that adopted by Greenish (*Pharm. Journ.*, 1881, [iii.], xi., 873), with certain modifications, and the method of plant analysis of Dragendorff. A third active constituent, besides the two already discovered in the root by Greenish, neriodorein and neriodorin, has thus been discovered, and named *karabin*, from *karabi*, the Bengali name of the plant.

The root gave the following percentages of the different extracts by Dragendorff's method:—Light petroleum extract, 2·88; ether extract, 1·38; absolute alcoholic extract, 3·40; aqueous extract, 5·81 per cent.

The ether extract was found to contain the *karabin*. This extract was partly soluble in absolute alcohol, giving a clear yellow solution, and on being evaporated to dryness left a brownish-yellow, sticky residue, *karabin*, which, on analysis, gave numbers corresponding to the formula $C_{21}H_{40}O_6$.

The alcoholic extract contained a substance identified as the neriodorin, and the aqueous extract contained the neriodorein. Neriodorein is readily soluble in water, neriodorein in boiling water only, while *karabin* is insoluble both in cold and boiling water. Neriodorein and neriordorin are insoluble in ether and benzene, but *karabin* dissolves readily in both. The colour reactions with concentrated sulphuric acid are also distinctive.

The author was also able to separate *karabin* by employing the following modification of Greenish's plan of analysis. The acidified aqueous solution of the alcoholic extract of the root was first shaken up with light petroleum, which removed a quantity of a viscid yellowish, oily substance. After the separation from the light petroleum, the solution was next agitated with ether *instead of chloroform*. The ethereal solution on evaporation left a brownish-yellow residue which gave all the reactions of *karabin*. The acidified fluid was next agitated with chloroform, which caused the separation of some oily looking globules which floated between the two layers of fluids; these were separated, washed, and evaporated to dryness; the residue gave all the reactions of neriodorein. The chloroform solution was then separated, and on evaporation left a golden-yellow brittle residue which satisfied all the tests for neriodorin.

The author considers that neriodorin is a variety of saponin. Neriodorein is very readily soluble in water, forming a pale yellow solution of neutral reaction which froths considerably on agitation. It has the acrid taste of saponin, and satisfied most of the tests for this widely distributed substance. It also closely resembles, in its behaviour with certain reagents, the variety of saponin described by the author and Warden (*Pharm. Journ.*, 1882, [iii.], xii., 302).

The author believes that both neriodorin and karabin are not glucosides, but possess the characters of a resin; neither contains nitrogen.

71. "*Change and Interaction in Organic Compounds.*" By A. LAPWORTH.

The apparently very general law to which the author has recently endeavoured to draw attention (*Proc.*, xvii., 2), receives a very simple explanation if it be supposed that isomeric change is due to dissociation and that *the dissociation between two atoms which leads to change in organic compounds exists, in general, only once in the*

molecule at any instant. Such a view leads to the $\alpha\gamma$- and $\alpha\beta$-rules, whether the labile group in an isomeric change never leaves the molecule as previously suggested (*Trans.*, 1898, lxxiii., 448), or whether ionisation occurs, for the above law holds true for weak electrolytes. In the author's opinion, therefore, the cause of change in general in organic compounds is probably to be sought for in a dissociation resembling ionisation, doubtless often in very small amount, a view arrived at independently of Euler (*Ber.*, 1900, xxxiii., 3202), and Zengelis (*Ber.*, 1901, xxxiv., 198), who used a similar assumption in order to explain the phenomena of hydrolysis and etherification.

The influence of a catalytic agent might be of very varying character, and can only be properly discussed in reference to particular cases. It may not only increase the velocity of change by raising the concentration of ions representing a labile group in isomeric change, or remove certain ions from the sphere of action by converting them into undissociated compounds, a suggestion which has been made by Euler and Zengelis, but, what is of equal importance, it may convert a molecule into an individual possessing the properties of a dissociated group or ion by supplying simpler groups with which it may unite, a process analogous to the formation of a complex ion by union of a simple ion with a neutral component (compare Abegg and Bödlander, *Zeit. Anorg. Chem.*, 1899, xx., 453).

It is to be observed that a molecule may also become a dissociated group by union with a dissociated part of a substance directly concerned in an interaction.

The atom from which a group has been removed will, of course, have an apparent valency of one unit less than that which it has in an undissociated compound; such an atom may be said to be "*subvalent*," or to represent a position of "*subvalency*." Whilst the atoms within a dissociated group will not change their relative positions in any way, the position of "subvalency" may conceivably be altered by a slight re-adjustment of the mutually attractive forces between the atoms; the removal of a group from one already dissociated does not mean a double dissociation, but the transference of the subvalency (and charge) to that group, and is analogous to the conversion of a complex ion into a simple ion and a neutral component. Perhaps, therefore, the above law should be stated—*No alteration of the relative positions of the atoms in a dissociated group can take place, and as a rule only one position of subvalency exists in such a group at any instant; in other words, it is usually subvalent.*

By means of the conception, the following rule may be deduced for some cases of interaction. If, during a reaction, a group M might be expected to become associated, even momentarily, with an atom R_α in the complex, $\cdot R_\alpha \cdot R_\beta : R_\gamma$, then the product may contain, not only substances with the grouping $R_\alpha M.R_\beta : R_\gamma$, but also, and sometimes exclusively, those with the grouping, $R_\alpha : R_\beta \cdot R_\gamma M$, or their tautomeric forms.

This rule at once gives some reason for the simultaneous formation of *ortho-* and *para*-derivatives when substitution occurs in a benzene mono-derivative, and for the similar but more complicated phenomena in the naphthalene series. Certain equations of considerable interest and importance may also be deduced. For example, if $X \cdot Y + A:B = AX \cdot BY$ is a possible reaction, then, expanding in terms of the rule, we obtain the following possibilities:—

$$X \cdot Y + A:B_\alpha \cdot B_\beta : B_\gamma = AX \cdot B_\alpha : B_\beta \cdot B_\gamma \quad .. \quad .. \quad .. \quad .. \quad (R)$$

at once recognisable as the form to which so much importance has been attached by Thiele.

$$X \cdot Y_\alpha \cdot Y_\beta : Y_\gamma + A:B = AX \cdot BY_\gamma \cdot Y_\beta : Y_\alpha \quad .. \quad .. \quad .. \quad .. \quad (S)$$

a form which is not translatable in terms of Thiele's rule. It is probably the basis of the Claisen reaction, the reactions between aldehydes and phenols, or the alkali salts of isonitro-compounds, and the change which occurs when *o*-acetylacetoacetic ester is converted into diacetylacetic ester by a trace of alkali. Expanding both B and Y, we obtain the form—

$$X \cdot Y_\alpha \cdot Y_\beta : Y_\gamma + A:B_\alpha \cdot B_\beta : B_\gamma = AX \cdot B_\alpha : B_\beta \cdot B_\gamma \cdot Y_\gamma \cdot Y_\beta : Y_\alpha \quad (T)$$

which finds examples in the interactions of ethyl sodio acetoacetate, malonate, cyanacetate, &c. (*iso*-forms), or $\alpha\beta$-unsaturated esters and ketones. In the above examples, X = K or Na, and $Y_\alpha = O$.

72. "*The Mechanism of the Claisen Reaction.*" By A. Lapworth.

The author takes the following view of this reaction in its simplest form:—

(1). A sodium ion unites with the carbonyl group of the ketone or ester to form a subvalent group which then loses a hydrogen ion,—

$$\dot{N}a + O:CR^1 \cdot CH_2R^2 \rightarrow Na \cdot O \cdot \dot{C}R^1 \cdot CH_2R^2 \rightarrow$$
$$\rightarrow Na \cdot O \cdot CR^1 : CHR^2 + \dot{H}.$$

The apparently direct replacement of a hydrogen atom in many esters, ketones, or even hydrocarbons (Thiele, *Ber.*, 1901, xxxiv., 68) is probably to be ascribed to the same cause; the reaction with hydrocarbons may be represented,—

$$\dot{K} + CR_2 : CR \cdot CHR_2 \rightarrow CR_2K \cdot \dot{C}R \cdot CHR_2 \rightarrow$$
$$\rightarrow CR_2K \cdot CR : CR_2 + \dot{H},$$

or, another possible type,—

$$CHR : CR_2 + \dot{K} \rightarrow CHRK \cdot \dot{C}R_2 \rightarrow CRK : CR_2 + \dot{H}.$$

(2). The metallic derivative then dissociates, part reacting with a subvalent group—produced by union of a sodium ion with ethyl oxalate, formate, &c.—as roughly represented by equation S (see preceding abstract).

$$Na \cdot O \cdot CR^1 : CHR^2 + CR^3(OEt) : O \rightarrow$$
$$\rightarrow [\dot{O} \cdot CR^1 : CHR^2 + \dot{C}R^3(OEt) \cdot ONa] \rightarrow$$
$$\rightarrow O:CR^1 \cdot CHR^2 \cdot CR^3(OEt) \cdot NaO \rightarrow$$
$$\rightarrow O:CR^1 \cdot CR_2 : CR^3 \cdot ONa + HOEt.$$

In the case of ethyl crotonate (*Proc.*, 1900, xvi., 132), the $\alpha\gamma$-rule must be applied a stage farther,—

$$Na \cdot O \cdot \overset{1}{C}(OEt) : CH \cdot CH : CH_2 + O : \overset{2}{C}(OEt) \cdot CO_2Et =$$
$$= Na \cdot O \cdot \overset{2}{C}(OEt)(CO_2Et) \cdot CH_2 \cdot CH : CH \cdot \overset{1}{C}(OEt) : O =$$
$$= Na \cdot O \cdot C(CO_2Et) : CH \cdot CH : CH \cdot CO_2Et + HOEt.$$

Exactly similar changes may be supposed to go on in the case of *o*-nitrotoluene, but here the nitro-group takes the place of the carbonyl group in the above cases. In *p*-nitrotoluene a further extension of the $\alpha\gamma$-rule is involved.

The action of hydrogen chloride in promoting the condensation of aldehydes with ketones, phenols, &c., may be ascribed to a similar series of changes, the hydrogen ions acting perhaps in this way:—

(1). $\dot{H} + O:C(CH_3) \cdot CH_3 \rightarrow H \cdot O \cdot \dot{C}(CH_3) \cdot CH_3 \rightarrow$
$\rightarrow H \cdot O \cdot C(CH_3) : CH_2 + \dot{H}.$

(2). $\dot{H} + O:CHPh \rightarrow H \cdot O \cdot \dot{C}HPh.$

(3). $\dot{O} \cdot C(CH_3) : CH_2 + \dot{C}H(OH)Ph \rightarrow$
$\rightarrow O:CMe \cdot CH_2 \cdot CH(OH)Ph \rightarrow$
$\rightarrow O:CMe \cdot CH : CHPh + HOH.$

Further experiments on diethyl oxalocrotonate (*Proc.*, 1900, xvi., 132), have strengthened the belief that it is the γ-oxalo-derivative; it has the normal molecular weight in acetic acid.

γ-Oxalocrotonic acid, $CO_2H \cdot C(OH) : CH \cdot CH \cdot CH \cdot CO_2H$, is a strong acid which is sparingly soluble in the ordinary organic media. It melts and decomposes at about 190°, being converted into α pyrone-α'-carboxylic acid. Its aqueous solution gives an intense black colour with ferric chloride which is not discharged by a large excess of hydrochloric acid.

Preliminary experiments on other $\alpha\beta$-unsaturated esters and ketones indicate that the following substances yield acidic compounds resembling ethyl oxalocrotonate: ethyl di-methylacrylate, ethyl β-chlorocrotonate, phorone, camphorone, and benzylidenemesityl oxide. The products, which have as yet been obtained only as oils, give intense

black colourations with ferric chloride; they are still under examination.

Ethyl α-methylacrylate, which does not contain the requisite grouping, gives no product of a similar kind, indicating that it is not the mere presence of the group $\cdot CH_2 \cdot C{:}C$ which is necessary.

73. "*A New Series of Di-mercuri-ammonium Salts.*" Part I. By P. C. Ray, D.Sc.

When a solution of mercuric nitrite is treated with ammonia in slight excess, a di-mercuri-ammonium nitrite of the formula $2NHg_2NO_2,H_2O$ is formed; if this compound be dissolved in hydrochloric acid, and the solution evaporated nearly to dryness, a white crystalline salt of the formula $NHg_2Cl,4HCl$ is obtained. Hydrobromic acid also yields the corresponding double bromide $NHg_2Br,4HBr$. Both haloid salts dissolve in water, and if the solutions be cautiously treated in the cold with dilute potassium hydroxide, the chloride and bromide, $2NHg_2Cl,H_2O$ and $2NHg_2Br,H_2O$, are formed respectively.

ROYAL SOCIETY CONVERSAZIONE.

On Wednesday evening last, the 8th May, a most successful Conversazione was held at the Society's Rooms at Burlington House, Piccadilly. The Fellows and Guests were received by the President, Sir William Huggins, K.C.B.

There was a large number of interesting and curious exhibits.

Mr. J. Mackenzie Davidson, M.B., showed some Stereoscopic Transparencies of Electrical Discharges. These photographs are taken by means of a small stereoscopic camera, and allow of the exact path of the discharge to be seen. In *single* photographs small bright dots are often seen, giving a "beaded" appearance. The stereoscopic views show that these "beads" are zig-zag discharges seen end-on.

A collection of Cloud Photographs by Commander D. Wilson-Barker, R.N.R., attracted some attention.

In the Council Room Mr. J. E. Barnard and Dr. Allan Macfadyen, B.Sc., &c., exhibited a number of Luminous Bacteria. These bacteria are a group of organisms, whose natural habitat is sea-water. They are the cause of the so-called phosphorescence to be seen at times on such objects as dead fish, meat, or other substances which are suitable soils for their growth and development. Their luminous properties are dependent on a supply of free oxygen, and a suitable percentage of a soluble chloride in the nutritive medium. The exhibit consists of artifical cultivations of these organisms on suitable nutrient soils, and shows their luminous properties, and the variations that occur under different physical conditions.

(1). Tube cultivations.
(2). Plate cultivations.
(3). Specimens showing illuminating power, *e.g.*, on printed matter.
(4). Influence of stream of oxygen on light production.
(5). Effect of agitation.
(6). Effect of electrolysis.

The Carl Zeiss Optical Works had several of their Stereoscopic Binocular Range-finders. This range-finder is founded on the same principle as their stereo-telescope, and is quite portable. The reading is taken direct from a scale within the instrument without calculations, giving the distances in metres. The range is from 75 to 3000 metres. The instrument can also be used for ascertaining the distance of a single light appearing only for a short time. A second scale is given by which the breadth and height of objects can be measured.

Prof. J. C. Bose's experiments on Binocular Alternation of Vision were very curious; by means of a specially made stereoscope each eye is impressed with the vision of a slanting bar of light; on closing the eyes these bars appear dark alternately—as one fades the other becomes apparent, and vice versa; this continues for some time.

A very serviceable Mechanical Interrupter for Induction Coils was shown by Dr. Dawson Turner. The contact is made and broken between two rollers immersed in paraffin; the rollers are mechanically rotated so that the burning at the break is distributed uniformly round the surfaces of contact which maintain their original form. It is adapted for working directly from the main.

Sir J. Norman Lockyer, K.C.B., exhibited some Photographs of the Spectra of *Nova Persei*. The photographs show that the spectra in the earlier stages consists of both bright and dark lines, the dark lines being displaced towards the more refrangible side of their normal positions, and indicating a great velocity of about 700 miles per second towards the earth. The bright line spectrum indicates a small movement away from the earth. The two superposed spectra indicate that *two* bodies are in question. The spectra show that as the star diminished in magnitude the continuous spectrum gradually became less intense, the bright metallic lines became fainter until the spectrum showed little more than the bright hydrogen and a few other chief lines. Details in the hydrogen lines themselves, indicating probable internal movements of the particles composing the Nova, are shown in the light curves of the hydrogen lines.

The Musical Arc exhibited by Mr. W. Duddell, and the Telegraphone, shown by the Syndicate bearing its name, both attracted a good deal of attention. The latter instrument, the invention of Mr. Poulsen, of Copenhagen, depends for its action upon the fact that the variations of the magnetic field of an electro-magnet are so accurately represented by the magnetisation of a steel-wire which is drawn through it, that if the wire be again passed through the field, currents exactly similar to those which produced the magnetisation of the wire are reproduced in the coils of the magnet. This principle has been applied to the reproduction of speech transmitted through an ordinary microphone transmitter.

During the evening three demonstrations took place in the Meeting Room. At 9.45, "Life-zones in the White Chalk," by Dr. Arthur Rowe; at 10.15, "Some Engineering Problems and their Solutions," by Mr. Francis Fox, C.E.; and at 11.0, "Kinematograph Diagrams, Illustrating Magnetic Fields," by Professor Silvanus P. Thompson.

NOTICES OF BOOKS.

Elements of Agriculture, for use in Schools. By James Bolton McBryde. Richmond, Va.: B. F. Johnson Publishing Co. 1901. Pp. 270, 12 mo.

American schoolbooks are not often reviewed in the columns of the Chemical News, but there is special propriety in naming this work, since it deals with agriculture from a scientific standpoint and its author is a chemist, having been for several years Chief Chemist of the Experiment Station at Knoxville, Tennessee, and at present connected with the Virginia Polytechnic Institute.

In the preface Mr. McBryde refers to the pressing need of agricultural instruction in the schools of the Southern States, and shows that seventy-five per cent of the seventeen million inhabitants cultivate the soil, whereas only one person in ten thousand is receiving any instruction in agriculture.

The book contains forty-six short chapters in seven parts, and gives in simple language the more important principles of scientific agriculture. Beginning with rudimentary studies of climate, plants (their composition and

manner of growth), soils (their classification and cultivation), manure and fertilisers, farm crops, animal production (stock foods, &c.), he writes in final chapters of the useful parts played by birds and by insects, of the care of forest trees, and the making of good roads, the importance of which he demonstrates. A pleasant feature of the book is the excellent manner in which abstract science is gradually introduced in the simplest language; the fundamental facts of chemistry and of botany are given, but these words themselves do not appear, so that the pupil is scarcely aware that he is studying these sciences.

In adapting chemical language to the comprehension of beginners the author rarely errs, but the reviewer does object to the use of the word "part" where atom is meant; on page 64 "CO_2" is said to signify "one part of carbon and two parts of oxygen." We imagine the author felt the difficulty himself, for in the very next sentence he accidentally gives the formula for water as "HO_2," and says this indicates "two parts of hydrogen and one part of oxygen." This small blemish can be corrected in a second edition.

The book contains a great many important truths, and corrects a number of prejudices and errors; it is intensely practical, constantly placing before the student the all-important "dollar and cent" question. Many of the statements are illustrated by facts drawn from personal experience, as well as from reports of high authorities.

As an introduction of the study of agriculture the work possesses great merit, and though primarily written for the southern portion of the United States it could be advantageously used in the Colonies of Great Britain and Ireland for the instruction of young classes, the members of which would find around them opportunities for supplementing the text by their own observations, as recommended by the author.

The book is well printed and illustrated with neat engravings; the proof-reading is generally clean, but on page 234 an amusing blunder occurs—for "Biographical Survey of the Department of Agriculture" read "Biological Survey." There is an index. H.C.B.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxii., No. 15, April 15, 1901.

New Researches on the Action of Hydrogen Peroxide on Silver Oxide.—M. Berthelot.—Hydrogen peroxide, when acting on silver oxide under certain conditions, forms first a dioxide, Ag_2O_2, which is extremely unstable, $Ag_2O+H_2O_2=Ag_2O_2+H_2O$. This equation represents the first phase of the phenomenon. This dioxide decomposes almost immediately, giving rise to two simultaneous reactions. A portion is resolved directly into silver and oxygen, $Ag_2O_2=Ag_2+O_2$, whilst another portion of the dioxide is decomposed in a less complete manner, being resolved into oxygen and silver protoxide; the latter combining with a further portion of the dioxide, $\left\{\begin{array}{l} Ag_2O_2 = Ag_2O + O \\ Ag_2O_2 + Ag_2O = Ag_4O_3 \end{array}\right.$. The following equation represents the second phase of the reaction:—$3Ag_2O+3H_2O_2=Ag_4O_3+Ag_2+O_2$. Unless great precautions are taken, the Ag_4O_3 decomposes spontaneously into Ag_2O and oxygen. The author examines all these reactions thermochemically.

Action of Radium Rays on Selenium.—Eugène Bloch.—In 1873, W. Smith discovered that the electric resistance of selenium diminished under the action of light. M. Perreau has generalised this property by showing that the Röntgen rays produce on selenium an action similar to that of light. The author examines the action of the rays from the new radio-active substances on selenium, and finds that the action of the rays of radium on selenium is of the same order of magnitude as the two preceding actions, though it is somewhat more slow. A selenium wire possessing at first a normal resistance of about 654,000 ω, fell in ten minutes to 640,000 ω under the action of the rays from radium; this being scarcely less than the effect of very feeble diffused light.

Examination of the Alkaloids by Micro-chemical Methods.—E. Pozzi-Escot.—The author's experiments were carried out on sulphate of strychnine, chlorohydrate of cocaine, brucine, sulphate of atropine, chlorohydrate of morphine, codeine, and sulphate of quinine. One per cent solutions, or saturated solutions in the case of slightly soluble alkaloids, were treated with picric acid on a glass slip and then examined with the microscope. The only picrate which was particularly characteristic was that of strychnine. As for the others, contrary to the statements of M. Popoff, the crystallisation took place with difficulty, and the crystals were ill-defined and not characteristic. The author therefore concludes that picric acid, the general reagent for alkaloids, has not the value as a micro-chemical reagent which M. Popoff has attributed to it.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxv., No. 1.

Measurement of the Speed of the Evolution of Gases. Application to the Voltameter.—André Job.—A test-glass with a foot is closed by means of a cork pierced with three holes, two of these holes are for the passage of the wires holding cylindrical electrodes of iron or nickel. The electrolyte is a 15 per cent solution of soda. The gas which is given off when the current passes goes through a tube with two arms; at one end a water manometer is adjusted, and at the end of the other arm there is fixed a piece of capillary thermometer tubing. When the current is made to pass, gas is given off, and we know from Graham's work on the transpiration of gases that, if the capillary tube is sufficiently long, the excess of pressure shown by the manometer will be proportional to the quantity of gas coming off; it will, therefore, at the same time, be proportional to the intensity (quantity) of the current. Thus we have a true ampèremeter.

New Method for the Separation of the Rare Metals which accompany Platinum.—E. Leidié.—Already inserted in full.

Action of Formate of Amyl on Cyanacetic Soda Ether.—E. Grégoire de Bollemont.—A mixture of 20 grms. of dry cyanacetic soda ether and 34 or 35 grms. of formate of amyl is heated for three hours on the water-bath in a flask fitted with a vertical condenser. The mass, which is colourless at first, becomes orange and then red, and changes into a thick liquid. The secondary products and the unacted on formate are eliminated by distillation *in vacuo*. The residue consists of a crystalline powder impregnated and coloured by certain very abundant oils, which are easily separated after adding boiling water. The aqueous solution, supposed to contain the sodium salt of formylcyanacetic ether, was decomposed by dilute sulphuric acid with the object of isolating the free ether. In this way a yellow oil was separated, which, when taken up with ether, dried over anhydrous sulphate of soda, and rectified *in vacuo*, gave hardly anything else than products of decomposition with abundant carbonaceous residues. There was, however, a trace of a well-crystallised body which distilled over at about 160° under 22 m.m., but it could not be obtained in a pure state.

Ethoxy- and Methoxymethene-cyanacetic Ethers.—E. Grégoire de Bollemont.

Oxymethene-cyanacetic Ethers.—E. Grégoire de Bollemont.

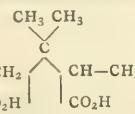
Action of Ammonia and Aniline on the Oxymethenecyanacetic Ethers and their Alcoylised Derivatives.—E. Grégoire de Bollemont.—Three very long papers, not suitable for abstraction.

On the Acid Suphuric Ethers of the Phenols.—Albert Verley.—The author has examined a general method for preparing these derivatives, especially those of eugenol, iso-eugenol, and vanilline. As a typical example, he describes the preparation of these latter derivatives and their application to the manufacture of vanilline.

Researches on the Tautomery of *o*-Benzoyl-benzoic Acid.—A. Haller and A. Guyot.—A consideration as to the correct formula for *o*-benzoyl-benzoic acid, in which the views of many other authors are discussed.

Separation of some Amidised Acids and their Active Components.—E. Fischer and A. Mouneyrat.—Not suitable for abstraction.

Experiments on the Synthesis of $\alpha\beta\beta$-Trimethylglutaric Acid.—G. Blanc.—The object of this research was to prepare synthetically $\alpha\beta\beta$-trimethylglutaric acid—



by a different method to that employed by W. H. Perkin and J. F. Thorpe (*Proc. Chem. Soc.*, 1899, p. 61). This result, however, was not achieved, but the synthesis was effected of a lactonic acid, $C_8H_{12}O_4$, which is of some interest from the point of view of the constitution of camphoric acid.

The Constitution of Camphoric Acid, and on one of the Migrations effected in its Molecule.—G. Blanc.—Already noticed.

Action of Bromine on Cinchonidine, and on two Bibromocinchonidine Isomers, α and β.—J. Galimard.—Using a method devised by M. Causse, the authors have attempted to bromise cinchonidine by the action of bromine in solution in hydrobromic acid. This process has given them two isomeric bromised derivatives, bibromocinchonidine α and bibromocinchonidine β, whose properties are here described.

Method of Analysis for the Estimation of Dextrose and Dextrin in Commercial Glucoses.—L. Lindet.—To estimate dextrose in the presence of dextrin, we can take the rotation of the mixture of the dissolved bodies, subtract from this the rotation given by dextrose to Fehling's solution, and calculate the weight of dextrin from the remaining rotation, always admitting that dextrin has a definite rotatory power. The author has, however, devised an improved method, which is based on an elementary analysis of the product; that is to say, on an estimation of the carbon, and on the rotation given by the dissolved product to polarised light. The correctness of the estimation of the carbon is beyond question; the only uncertainty rests on the exact rotatory power of dextrin adopted, that of dextrose (52·5°) being incontestable. 0·4 grm. of the material is burnt in the presence of oxide of copper, and from the weight of the carbon found the quantity of carbohydrates present is deduced, using the formula $C_6H_{12}O_6$. We then take about 5 grms., and, as above, calculate the contents of hydrates of carbon; let this weight be called S. We then obtain an equation, $S = D + d$; where D is the weight of dextrose, and d the weight of dextrin. This done, the material is dissolved in 100 c.c. of water, and the rotation taken with a ray of yellow light. The rotation observed, R, is equal to the sum of the rotations of dextrose and dextrin. Now each of these rotations can be determined by the formula $\rho = \frac{p\,a\,l}{v}$. We then use the following equation:—

$$\frac{D \times \alpha \times 2}{100} + \frac{d \times \alpha' \times 2}{100} = R,$$

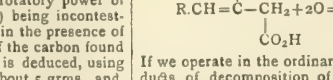
$$\frac{D \times 52{\cdot}5 \times 2}{100} + \frac{d \times 195 \times 2}{100} = R.$$

We then successively replace D and d by their value in functions of S, and obtain the weight of dextrose, and of dextrin reckoned as dextrose. This latter is reduced to its true weight by multiplying by 0·9.

MISCELLANEOUS.

Royal Institution.—The Annual Meeting of the Members of the Royal Institution was held on May 1st, Sir James Crichton-Browne in the Chair. The Annual Report of the Committee of Visitors for the year 1900, testifying to the continued prosperity and efficient management of the Institution, was read and adopted, and the Report on the Davy-Faraday Research Laboratory of the Royal Institution, which accompanied it, was also read. Forty-seven new Members were elected in 1900. Sixty-three Lectures and nineteen Evening Discourses were delivered in 1900. The Books and Pamphlets presented in 1900 amounted to about 262 volumes, making, with 653 volumes (including Periodicals bound) purchased by the Managers, a total of 915 volumes added to the Library in the year. Thanks were voted to the President, Treasurer, and the Honorary Secretary, to the Committees of Managers and Visitors, and to the Professors, for their valuable services to the Institution during the past year. The following gentlemen were unanimously elected as Officers for the ensuing year:—President—The Duke of Northumberland; Treasurer—Sir James Crichton-Browne; Secretary — Sir William Crookes; Managers — Sir Frederick Abel, Bart., Sir William de W. Abney, Sir James Blyth, Bart., Sir Frederick Bramwell, Bart., Dr. Thomas Buzzard, Viscount Gort, Dr. Donald William Charles Hood, the Right Hon. Lord Kelvin, Sir Francis Henry Laking, Mr. Hugh Leonard, Dr. Frank McClean, Mr. James Mansergh, Mr. George Matthey, Mr. William Hugh Spottiswoode, and the Right Hon. Sir James Stirling; Visitors—Sir Andrew Noel Agnew, Bart., Dr. Charles Edward Beevor, Mr. William Henry Bennett, Dr. Francis Elgar, Mr. Joseph G. Gordon, Dr. James Dundas Grant, Lord Greenock, Mr. Maures Horner, Mr. Henry Francis Makins, Sir Thomas Henry Sanderson, Mr. William Stevens Squire, Mr. Harold Swithinbank, Mr. John Jewell Vezey, Mr. Roger William Wallace, and Mr. James Wimshurst.

Formation of Oxalacetic Acid by Oxidation by means of Permanganate in Alkaline Solution.—R. Fittig.—The oxidation of the itaconic acids partially transforms them into bibasic oxylactonic acids, while the remainder obeys the general equation, and gives oxalacetic acid,—



If we operate in the ordinary manner, we only obtain products of decomposition of oxalacetic acid. Thus, dimethylitaconic acid gives acetone and oxalic and acetic acids. But if we repeat this oxidation by permanganate of potash in slightly alkaline solution at 0°, and then, after filtering off the MnO_2 and acidulating with H_2SO_4, we exhaust with ether to remove the unoxidised original acid, we obtain oxalacetic acid in the aqueous solution. By

the careful addition of concentrated sulphuric acid, the acid passes over in a form soluble in ether, from which it is afterwards extracted by evaporation. No other product is formed besides acetone and oxalacetic acid. The reaction may be therefore briefly formulated thus:—

$$CH_3>C=C<\begin{matrix}CO_2H\\CH_2.CO_2H\end{matrix}+2O=$$
$$=\begin{matrix}CH_3\\CH_3\end{matrix}>CO+OC<\begin{matrix}CO_2H\\CH_2.CO_2H\end{matrix}.$$

The determinations made on this body exactly confirm those given by Fenton and Jones.—*Berichte*, vol. xxxiii., p. 1295.

The Acetylation of Acetylacetic Ether.—L. Claisen and E. Haase.—The chlorides of the acids react on the soda derivatives of the β-ketonic ethers, giving principally acidylised derivatives of the type $CO—CH(COR)—CO_2C_2H_5$; their isomers, $C(O.COR)=CH—CO_2C_2H_5$, are obtained, on the contrary, by acting with the chloride of the acid on δ-ketonic ether in the presence of pyridine or an analogous base. The authors have applied this last method to the case of acetylacetic ether. They obtained the ether, $CH_3.C(OCOCH_3)=CH.CO_2C_2H_5$, by dropping chloride of acetyl (1·5 mols.) into a well-cooled mixture of acetylacetic ether (1 mol.) and anhydrous pyridine (2 mols.). After standing for two days, the acetyl-derivative is isolated by means of ether, the ethereal solution is washed with dilute soda to eliminate the excess of acetylacetic ether, then with dilute sulphuric acid and with water; it is then dried and distilled. The pure product distils at 104—105° at 10 m.m., at 112—113° at 17 m.m., and at 214—216° at the normal pressure, with partial decomposition; the return is 104 per cent of the weight of the acetylacetic ether. It is insoluble in the alkalis, which only attack it slowly. The same treatment has been applied to diacetylacetic ether, $(CH_3.CO)_2.CH.CO_2C_2H_5$; it gave the derivative $CH_3—C(OCOH_3)=C(COCH_3)—CO_2C_2H_5$. The product is fractionated at 15 m.m. without washing; the return is 70—80 per cent. It boils at 142—144° at 10 m.m., at 145—147° at 13 m.m., and at 148—150° at 15 m.m. It is a yellowish liquid decomposed instantly by water and by alkalis. It is obtained in very small quantities by the action of chloride of acetyl on diacetylacetic ether.—*Berichte*, vol. xxxiii., p. 1242.

The Compounds of Carbonic Oxide with Iron, and their Importance with regard to Water-gas.—M. van Breukeleveen and A. Ter Horst.—Roscoe and Sendder have already observed that water-gas kept for some time in an iron cylinder at a pressure of eight atmospheres contains a volatile ferric compound. Strache and Dicke, on the other hand, have shown that, under certain circumstances, the use of water-gas, even when not under pressure, leaves a brown powder on the Auer mantles which quickly renders them unserviceable. But these two authorities did not agree as to the cause of the phenomenon. According to Strache, iron carbonyl is formed near the generator, at the point where the gas comes in contact with the red-hot iron. Dicke, on the other hand, asserts that this product is formed in the iron pipes by the action of the gas on the iron in the cold. The authors have taken up the examination of this subject, and they confirm Dicke's opinion and have proved it to be correct by means of a series of experiments. The gas taken at the factory, or gas which has passed through lead pipes only, does not contain any iron carbonyl; but gas which has passed through iron pipes, or has even simply been in contact with polished iron for a week, contains this body. This action is in strict relation to the proportion of CO present; a synthetic mixture of CO_2, O, CO, H, and N gave the same results. To do away with this inconvenience, it is proposed to coat the interior of the pipes with tar, or to pass the gas through H_2SO_4, or to decompose the $Fe(CO)_5$ by means of heat; the authors have used $KMnO_4$ with success on the small scale.—*Revue Tr. Ch.*: *P.-B.*, [vol. xix., p. 27.

MEETINGS FOR THE WEEK.

Monday, 13th.—Society of Arts, 8. (Cantor Lectures). "Alloys," by Sir William Chandler Roberts-Austen, K.C.B., F.R.S., and T. Kirke Rose, D.Sc.

Tuesday, 14th.—Royal Institution, 3. "On Cellular Physiology, with special reference to Enzymes and Ferments," by Allan Macfadyen, M.D., B.Sc.

Wednesday, 15th.—Society of Arts, 8. "Syntonic Wireless Telegraphy," by Guglielmo Marconi.

—— Microscopical, 7.30. An Exhibition of Aquatic Life.

—— Institution of Mining and Metallurgy 8. "The Assaying of Complex Gold Ores," by Ernest A. Smith, Assoc.R.S.M. "Notes on Brine and Oil Wells in Western China," by J. V. Burne Murdoch. "Vein Structure at the Reynolds Mine, Georgia," by G. E. Collins. "Cherroloque Tin Mines and Alluvial Deposits, Bolivia," by Malcolm Roberts.

Thursday, 16th.—Royal Institution, 3. "Arthur Sullivan" (with Vocal and Instrumental Illustrations), by Sir Alex. Campbell Mackenzie, Mus.Doc.

—— Chemical, 8. "The Nutrition of Yeast" (Part III.), by A. L. Stern, D.Sc. "Derivatives of Methylorcinol," by H. J. H. Fenton and Miss Mildred Gostling. "The Preparation and Optical Inversion of Optically Active Nitrogen Compounds, Dextro- and Lævo-α-benzylphenylallylmethylammonium Salts," by W. J. Pope and A. W. Harvey.

—— Society of Arts, 5 (at the Imperial Institute, South Kensington). "The Town and Island of Bombay—Past and Present," by L. R. Windham Forrest.

Friday, 17th.—Royal Institution, 9. "Turkish Kurdistan," by Earl Percy, M.P.

—— Society of Arts, 8. (Howard Lectures). "Polyphase Electric Working," by Alfred C. Eborall, M.I.E.E.

Saturday, 18th.—Royal Institution, 3. "The Rise of Civilisation in Egypt," by Prof. W. M. Flinders Petrie, D.C.L.

NOTES AND QUERIES.

**** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Determining Naphthaline.—I would be pleased if some one of your readers would give a method of determining naphthaline in dead oil distilled from coal-tar.—Donald Davidson, Detroit, Mich.

TO MANUFACTURERS OF CHEMICAL, &c., APPARATUS.

The BECKENHAM URBAN DISTRICT COUNCIL invite Tenders for the Supply of the necessary APPARATUS for teaching Chemistry and Physics.

Tenders (by Discount from published Price List) to reach the undersigned not later than 4 p.m. on Monday, the 20th inst.

(By Order) F. STEVENS,
May 9th, 1901. Clerk of the Council.

INSTITUTE OF CHEMISTRY
OF GREAT BRITAIN AND IRELAND.
Incorporated by Royal Charter.

NOTICE IS HEREBY GIVEN that the INTERMEDIATE EXAMINATION and the FINAL EXAMINATION for the ASSOCIATESHIP of the Institute of Chemistry (A.I.C.) for persons desirous of qualifying themselves to be Public and Technical Analysts, will commence at the Laboratories of the Institute, 30, Bloomsbury Square, London, W.C., on Tuesday, July 2, 1901.

The Arrangements for the Examinations depend upon the number of Candidates; therefore, Candidates for the Final Examination may be required to present themselves from Tuesday, 9th, to Friday, July 12, 1901.

The Final Examination in Branch F (Biological Chemistry) will be held in October.

Notice will be given to all Candidates whose applications for examination are received and accepted by the Council not later than Wednesday, June 5, on which day the examination lists will be closed.

Forms of application and further particulars can be obtained from the Registrar.

(By Order of the Council)
30, Bloomsbury Square, London, W.C. RICHARD B. PILCHER, Registrar and Secretary.

"The Regulations for Admission to Membership" may be obtained from Messrs. Blundell, Taylor, and Co., 173, Upper Thames Street, London, E.C., price One Shilling.

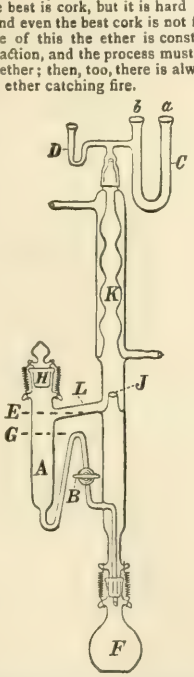
THE CHEMICAL NEWS.

Vol. LXXXIII., No. 2164.

NEW FAT-EXTRACTION APPARATUS.

By Dr. W. JERWITZ.

Everyone who has worked with the Soxhlet fat-extraction apparatus is aware of the difficulty of obtaining a tight joint between the condenser and the extractor, on account of the great volatility of the ether. India-rubber stoppers cannot be used, because they become partially dissolved in ether, and besides spongy substances swell up in strong ether vapour. The material that has been found to be the best is cork, but it is hard to obtain it of good quality, and even the best cork is not free from pores. In consequence of this the ether is constantly escaping during the extraction, and the process must be interrupted to put in fresh ether; then, too, there is always the danger of the escaping ether catching fire.



Another objection to the use of cork is that it soon wears out, becomes loose, and must often be renewed.

The apparatus has none of these disadvantages, for by means of having the extractor joined to the side of the condenser, it becomes possible to make the extractor and condenser in one piece, thus dispensing with all connections of cork, &c. As the stability of the apparatus much depends on the way of fixing it, the apparatus has been supplied with two clamps especially constructed for it, which give a solid, safe, but not absolutely rigid grip, so that the apparatus is not likely to be crushed in handling.

The clamps allow the apparatus to be turned round its own length axially, and the necessity of taking it from its stand after once being fixed never arises; this will certainly in a great degree minimise the danger of breakages.

The tube of calcium chloride which is attached prevents the entrance of moisture. To do away with any danger of an explosion, which might take place if the calcium chloride tube should chance to get choked, the steam in that case can get out through the second little U-tube which is merely filled with mercury.

So that the condenser and the fat flask need not be connected by cork or rubber, the flask is slid into the other and held there by two spiral springs. Thus no support need be placed under the flask, and there is no danger of the neck being broken by striking it against it.

The two accompanying clamps are to be fastened to a wooden partition or a board fixed to the wall. Place the open clamp vertically above the other and a suitable distance from it, say 35 to 40 c.m. = about 15 inches. Slide the top end of the condenser through the top clamp, and let the bottom end rest on the lower one. Connect the condenser to the water pipe in the usual way. Then connect with the condenser the two U-tubes—a larger one, C, and a smaller one, D—after having greased the edge of the glass, which may be done without any danger to the analysis. C is filled with calcium chloride and closed at *a* by a stopper of wadding or a perforated cork; it is made air-tight at *b*. D contains a mercury trap and is likewise closed by a piece of wadding.

To start the apparatus attach the flask, F, to the bottom end of the apparatus with an ungreased joint by means of the enclosed spiral springs. Place the fat-cartridge which contains the material to be extracted in A, and fill the extractor, A, to a height of about E with anhydrous ether, having the stopcock, B, closed. Then put in the glass stopper, H, which for safety is also held on by two spiral springs. Open the cock at B, which sets the syphon working, and the fat-saturated ether will flow from A into F.

The condenser is now completely arranged. Heat F by a water-bath; do not support F, but allow it to hang free in the water. It is advisable to govern the temperature of the water-bath by a thermo-regulator. This, if once introduced, never allows the temperature to rise above the desired point, and thus makes other precautions unnecessary. Without this it is difficult, even with the greatest attention, to keep the temperature uniform, especially when the pressure of the gas varies, as is frequently the case.

The fat remains behind in F, whilst the ether distils off through J into the condenser, K, and is condensed. The ether flowing down the windings of the condenser is prevented from flowing back through J into F, but gets back through L into A, and acts over again on the fat-cartridge. As soon as A is filled up to G the ether again flows off and the process is repeated.

When the extraction is complete close the stopcock B again, and the ether will collect in A. When all the ether has been distilled over, take away the flame, disconnect F, and let the ether flow off through the stopcock B into another vessel; then take A away and remove the cartridge by means of a long tongs or a wire hook.

If the calcium chloride tube, *b*, should become choked the steam can get out through D, which acts as a safety valve.

Laboratory,
74, Rogerson's Quay, Dublin.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 6th inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Dr. D. W. Buxton, Mr. W. I. Last, Mr. J. Stirling, Mr. H. P. Whiting, were elected Members. It was announced that His Grace the President had nominated the following Vice-Presidents for the ensuing year:—Sir Frederick Bramwell, Bart., The Right Hon. Sir James Stirling, Sir William Abney, K.C.B., The Right Hon. Lord Kelvin, G.C.V.O., Mr. George Matthey, Mr. Frank McClean, Sir James Crichton-Browne, Treasurer, and Sir William Crookes, Hon. Sec.

THE PREPARATION OF URANIUM.

By J. ALOY.

The most convenient methods for the preparation of uranium are the reduction of the anhydrous oxides, either by carbon or by other metals.

Electric Furnace Method.

In a series of papers presented to the Academy of Sciences, M. Moissan describes the conditions under which uranium and its carbide are formed in the electric furnace (*Comptes Rendus*, vol. cxv., p. 1031; vol. cxvi., p. 347; vol. cxxii., p. 274). He used an arc of 500—800 ampères, and 45—55 volts. The densities of such currents being much greater than those generally in use, it seemed to me to be of interest to try if uranium could be prepared by means of currents of much less strength. With this object I undertook two series of experiments, the first with 15—25 ampères, and the second with 100—200 ampères. In the furnace I placed a mixture of U_3O_8 in slight excess, and sugar charcoal. The temperature of the mass being a function of the dimensions of the apparatus, I constructed a series of small furnaces with bricks of dressed lime.

The first experiments gave me very mediocre results; with the maximum current of 25 ampères, and by reducing the cavity of the furnace to 4 or 5 c.c., I obtained in the immediate neighbourhood of the electrodes fragments of carbide, the weight of which did not exceed 4 or 5 decigrammes.

The results in the second case were, on the other hand, fairly satisfactory; even with 100 ampères the arc, which was very small at the commencement of the experiment, could soon be considerably lengthened, and after about ten minutes the experiment was finished; in the cavity of the furnace I found, after cooling, several grains of carburised uranium.

I found, however, on varying the conditions that not more than 30 or 40 grms. of material should be operated upon; a current of 150 ampères gave 20 to 25 grms. of uranium in a few minutes, and may be considered as sufficient for the preparation of small quantities of the metal.

The conditions for getting the best returns were obtained with 50 to 60 volts.

Reduction of the Oxides by Metals.

Peligot has already pointed out the possibility of reducing the oxides of uranium by means of potassium, but the difficulty of obtaining a homogeneous mixture renders this method impracticable. I tried to effect the same reduction with the help of metals which, besides having a great affinity for oxygen, also have the advantage of being easily worked; I succeeded with magnesium and aluminium.

A mixture of the green oxide U_3O_8 with one of these metals reacts under the influence of heat alone. The reduction takes place at a dull red heat with magnesium, and is very violent; a bright red heat is required in the case of aluminium, but the reaction is much more regular. If we prevent the subsequent oxidation of the metal by operating in an inert atmosphere we can prove the presence of uranium by the action of dilute hydrochloric or sulphuric acids which give green solutions, and which do not attack the oxides U_3O_8 and UO_2.

But these methods, like that of Peligot, must be looked upon simply as methods of production, as the metal cannot be afterwards separated from the gangue.

Uranium can be separated by fusion by using a modification of Goldschmidt's method. It suffices to substitute the oxide UO_2, which is much more easy to reduce, and to combine the action of internal heat with that which is produced by the reaction itself. In a fire-clay crucible an intimate mixture of sugar-charcoal and the oxide UO_2, prepared at as low a temperature as possible by the reduction of the oxide $UO_3.H_2O$, is placed; after heating the mass to dull redness the reaction is started as in the case of the aluminothermy of metals, by means of a small cartridge formed of magnesium and binoxide of barium. The reaction starts immediately throughout the mass, and the melted metal collects at the bottom of the crucible in the form of an ingot.

Uranium thus prepared is not absolutely pure, it contains a small quantity of aluminium; nevertheless, I have obtained samples containing as much as 96 to 97 per cent of uranium.

M. Moissan has already shown (*Comptes Rendus*, vol. cxiii., p. 2), the possibility of obtaining alloys of uranium and aluminium by introducing the oxide U_3O_8 into a bath of melted aluminium.—*Bull. Soc. Chim.*, Series 3, vol. xxv., No. 7.

THE VOLUMETRIC ESTIMATION OF COPPER AS THE OXALATE, WITH SEPARATION FROM CADMIUM, ARSENIC, TIN, AND ZINC.*

By CHARLES A. PETERS.

(Continued from p. 222).

In the quantitative separation of copper as the oxalate the method of treatment was in general as follows:—Copper sulphate in 50 c.m.³ of water was thrown down by the addition of dry oxalic acid to the hot solution, and, after standing over night, the precipitate was filtered on asbestos, washed two or three times with small amounts of cold water. The precipitate, still in the crucible, was returned to the beaker in which precipitation took place, 5 or 10 c.m.³ of dilute sulphuric acid (1 : 1) were then added together with a convenient amount of water, and, after heating the liquid to boiling, the oxalic acid was titrated with permanganate, the oxalate of copper dissolving readily as fast as the excess of oxalic acid is removed by the permanganate. The precipitate may also be dissolved in 10 c.m.³ of strong hydrochloric acid (Gooch and Peters, *Am. Journ. Sci.*, 1899, vii., 461; Chemical News, vol. lxxx., p. 78), 0·5 grm. manganous chloride added, and titrated at 30—50°. Experiments 4 and 5 were conducted after this manner. In Table III., A, are recorded results of the quantitative tests of the method.

In Experiments 1 to 4, deficiencies are found in the amounts of oxalate precipitated at different degrees of dilution and by different amounts of the precipitant which are in agreement with the results obtained in the preliminary work; the results of Experiments 5 to 9, in which 0·5 grm. and 1·0 grm. of oxalic acid act in a total volume of 50 c.m.³, show the precipitation to be essentially complete under these conditions.

To study the insolubility of the copper oxalate in nitric acid, the experiments in Section B (Table III.) were made.

In Experiments 10 to 13 amounts of oxalic acid varying from 0·5 grm. to 3·0 grms. appear to precipitate the copper completely in the presence of 5 c.m.³ of strong nitric acid. In Experiment 14 the amount of oxalic acid used was not sufficient to throw down all the copper in the presence of 10 c.m.³ of nitric acid, but the copper does come down completely in the presence of the large amount of the nitric acid upon the addition of more oxalic acid, as seen in Experiments 15 and 16. In Experiments 17 and 18, with a larger volume of water and a larger absolute amount—though approximately the same percentage—of nitric acid present as in Experiments 10 to 13, there is a slight loss of copper; but in Experiments 21 and 22, when the amount of nitric acid is reduced to 5 c.m.³ in the

* Contributions from the Kent Laboratory of Yale University. From the *American Journal of Science*, vol. x., No. 59.

Table III.

	CuO taken as $CuSO_4$. Grm.	Oxalic acid. Grms.	HNO_3 (sp.gr. 1·40). C.m.³.	Volume at precipitation. C.m.³.	CuO found. Grm.	Error. Grm.	Details of filtration.
				A.			
1.	0·0372	0·15		100	0·0286	−0·0086	
2.	0·1860	0·50		125	0·1831	−0·0029	
3.	0·0398	0·50		50	0·0376	−0·0022	
4.	0·1860	1·0		150	0·1834	−0·0026	
5.	0·1860	0·5		50	0·1864	+0·0004	
6.	0·1860	0·5		50	0·1866	+0·0006	
7.	0·1860	0·5		50	0·1866	+0·0006	
8.	0·1860	1·0		50	0·1866	+0·0006	
9.	0·0398	1·0		50	0·0391	−0·0007	
				B.			
10.	0·1860	0·5	5·0	55	0·1859	−0·0001	
11.	0·1860	0·5	5·0	55	0·1860	±0·0000	
12.	0·1990	2·0	5·0	55	0·1989	−0·0001	
13.	0·1990	3·0	5·0	55	0·1990	±0·0000	
14.	0·1990	2·0	10·0	60	0·1971	−0·0019	
15.	0·1990	3·0	10·0	60	0·1987	−0·0003	
16.	0·1990	3·0	10·0	60	0·1985	−0·0005	
17.	0·1990	5·0	12·0	130	0·1977	−0·0013	
18.	0·1990	5·0	12·0	130	0·1975	−0·0015	
19.	0·1990	5·0	25·0	130	0·1837	−0·0153	
20.	0·1990	5·0	25·0	130	0·1831	−0·0159	
21.	0·1990	5·0	5·0	130	0·1983	−0·0007	
22.	0·1990	5·0	5·0	130	0·1988	−0·0002	
				C.			
23.	0·1990	2·5	5·0*	65	0·1971	−0·0029	
24.	0·1990	2·0	5·0	65	0·1981	−0·0019	
				D.			
25.	0·1990	2·0		50	0·1984	−0·0006	Filtered hot, immediately.
26.	0·2030	2·0		50	0·2025	−0·0005	" " "
27.	0·1990	1·0		50	0·1990	±0·0000	Filtered after cooling; stood fifteen minutes.
28.	0·1990	1·0		50	0·1987	−0·0003	" " " "
				E.			
29.	0·1990	2·0	5·0	55	0·1943	−0·0047	" " " "
30.	0·1990	2·0	5·0	55	0·1969	−0·0021	Stood two and a half hours.
31.	0·1990	2·0	5·0	55	0·1973	−0·0017	Stood six hours.
32.	0·1990	2·0	5·0	55	0·1989	−0·0001	Stood sixteen hours.

* About 9 grms. of ammonium nitrate present in addition to the 5 c.m.³ of nitric acid.

larger total volume, the results are normal. Experiments 19 and 20 show the increased loss when still larger amounts of nitric are present. These facts would make it seem best to limit the absolute amount of nitric in solution to about 5 c.m.³.

One observation may well be noted here; namely, that while ½ grm. oxalic acid is all that is needed for the complete precipitation of the copper in the presence of 5 c.m.³ strong nitric acid, still the oxalic acid may be added up to the point of saturation of the solution. More than this causes difficulty, owing to the fact that a large amount of water is necessary to wash the precipitated oxalate. About 2·0 grms. of oxalic acid to 50 c.m.³ of water is a convenient proportion.

In Experiments 23 and 24, 5 c.m.³ of nitric acid were neutralised with ammonium hydroxide before adding the 5 c.m.³ strong nitric acid in excess. The results show the solubility of copper oxalate in ammonium nitrate and exclude the possibility of such a procedure in this work.

Some experiments were made to show the time necessary for the complete precipitation, both in the presence and absence of nitric acid. The record of such work is given in Sections D and E (Table III.).

The results in Section D would seem to show that a solution containing copper may be precipitated hot as the oxalate and filtered either hot or after cooling with a very slight loss. Tests of the filtrates made with potassium ferrocyanide confirmed these results. When nitric acid is present, however, the mixture must stand after the addition of the precipitant. In Section E the gradual decrease of the minus error is noticed as the time of standing is extended, the precipitation being practically complete upon standing over night.

(To be continued).

SOME PRINCIPLES AND METHODS OF ROCK ANALYSIS.*

By W. F. HILLEBRAND.

(Continued from p. 220).

XX. *Alkalis.*

The Lawrence Smith Method.

The various methods for getting at the alkalis in insoluble silicates differ more in the mode of attack of the mineral powder, and in the immediately subsequent treatment, than in the final stages. With very few exceptions, since the early days of the Survey's existence, all alkali determinations have been made by the method of J. Lawrence Smith (*Amer. Journ. Sci.*, 1871, Second Series, vol. l., p. 269: *Amer. Chemist*, 1871, vol. i.; *Anal. Chem. und Pharm.*, 1871, vol. clix., p. 82), which is far more convenient than and fully as accurate as those in which decomposition is affected by hydrofluoric and sulphuric acids, or by bismuth, lead, or boric oxides. One of its chief advantages is the entire elimination of magnesia at the start.

* *Bulletin of the United States Geological Survey*, No. 176.

Decomposition of the powder is effected by heating it with its own weight of ammonium chloride, and eight times as much precipitated calcium carbonate.

The ammonium chloride used must be purified, preferably by sublimation, or made by neutralising pure ammonia by pure hydrochloric acid, and the calcium carbonate is best obtained from pure calcite by solution and re-precipitation. However obtained, this last is rarely free from alkalis, which must be estimated once for all in a blank test in order to apply a correction. Eight grms. of the carbonate will contain usually from 0·0012 to 0·0016 grm. of alkali chlorides, almost entirely the sodium salt, but the amount has been brought down to half the above by very long washing. This correction may be admitted at once to be a defect of the method, but it is one easily applied with safety.

The ignition may be made in a covered crucible of ordinary shape, and of about 20 to 30 c.m.^{3} capacity, heated to dull redness for not more than two-fifths of its height, but the heat has to be kept so low in this case to avoid loss by volatilisation that perfect decomposition is not always assured. Hence, to avoid waste of time in very fine grinding, the form of crucible with cap originally advocated by Smith is very much to be preferred, since it permits, when set at an angle through an opening in the side of a fire-clay cylinder, of the application of the full heat of two burners, and perfect decomposition invariably results without the need of extraordinary care in grinding. The crucible used in this laboratory (Fig. 14)

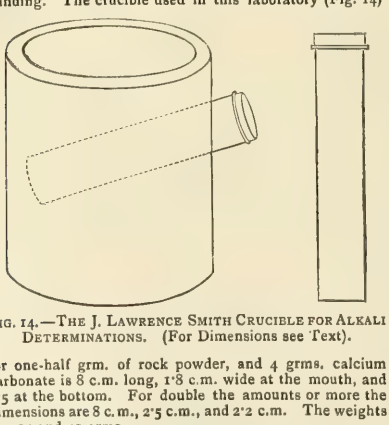


Fig. 14.—The J. Lawrence Smith Crucible for Alkali Determinations. (For Dimensions see Text).

for one-half grm. of rock powder, and 4 grms. calcium carbonate is 8 c.m. long, 1·8 c.m. wide at the mouth, and 1·5 at the bottom. For double the amounts or more the dimensions are 8 c.m., 2·5 c.m., and 2·2 c.m. The weights are 25 and 40 grms.

Treatment of the Mineral Powder.—Perfectly satisfactory results are to be obtained with but half a grm. of rock powder. This is weighed out, ground down somewhat finer in a large agate mortar, mixed with its own weight of sublimed ammonium chloride, and the two thoroughly ground together. Then nearly all of 4 grms. of calcium carbonate is added, and the grinding continued till a thorough mixing has resulted. The contents of the mortar are transferred to the long crucible, the rest of the carbonate being used for rinsing off mortar and pestle. The crucible is then capped and placed in a clay cylinder (Fig. 14), or through a hole in a piece of stout asbestos board clamped in a vertical position, and heated for about ten minutes by a low, flat flame placed at considerable distance beneath. As soon as the odour of ammonia is no longer perceptible the nearly full flame of two Bunsen burners is applied, and continued for forty to fifty minutes.

* To avoid the formation of a melted cake with silicates very high in iron it is advisable to increase the proportion of calcium carbonate.

The sintered cake* detaches readily from the crucible as a rule; if not, it is softened up in a few minutes by hot water, and digested in a dish until thoroughly disintegrated. It is first washed by decantation, and any lumps are broken up by a pestle, then thrown on the filter, and well washed with hot water. The residue should dissolve completely in hydrochloric acid without showing the least trace of unattacked mineral, not even of quartz.

Separation of Calcium and Sulphuric Acid.—All but a trifling amount of the calcium is separated at boiling heat in a large platinum dish by double precipitation by ammonia and ammonium carbonate. The combined filtrates are evaporated to dryness, and the ammonium salts are carefully driven off. From the aqueous solution of the residue—but a few cubic centimetres in bulk—the rest of the calcium is thrown out by ammonia and ammonium oxalate, this last being more effective than the carbonate. The filtrate, caught in an untared platinum crucible or small dish, is evaporated to dryness, and gently ignited; the residue is moistened with hydrochloric acid to decompose any alkali carbonate that may have been formed, again evaporated, ignited, and weighed. On solution in water a few tenths of a milligrm. of fixed residue is invariably left, which should be collected, ignited, and weighed in the same crucible or dish in order to arrive at the weight of the chlorides.

If the rock contains sulphur this will be in part found with the chlorides as sulphate. Therefore, if the sulphur is at all considerable in amount it must be removed by a drop of barium chloride before the final precipitation of the calcium. The excess of barium is removed by ammonium carbonate, and the last of the calcium by ammonium oxalate, as above. If the sulphur is not thus removed there is danger, if not certainty, of the potassium-platinic chloride carrying sodium sulphate. A faint reaction for sulphate can usually be obtained, anyway, if the evaporations have been made on a water-bath heated by gas.

Precipitation of Potassium.—To the solution of the chlorides in a small porcelain* dish an excess of platinic chloride solution is added. The dilution should be such that when heated on the water-bath any precipitate that may form wholly re-dissolves. Evaporation is then carried on till the residue solidifies on cooling. It is then drenched with absolute alcohol,† or with that of 80 per cent strength, filtered by decantation through a very small filter, and washed by decantation with alcohol of the same strength. The precipitate is not brought on to the filter more than can be avoided. Dish and filter are then dried for a few minutes to remove adhering alcohol, the contents of the former are transferred to a weighed platinum crucible or very small dish, and what still adheres to the porcelain is washed through the filter with hot water into the weighed receptacle. This is now placed on the water-bath, and afterwards heated to 135° C. in an air-bath. The factor used for reduction of K_2PtCl_6 to 2KCl is 0·307, and of 2KCl to K_2O, 0·632.

Lithium.

After separation of the potassium platinic chloride, the alcoholic filtrate is evaporated and tested spectroscopically for lithium. This element is almost invariably present, but almost never in amount to warrant quantitative estimation. Should it be so, however, the very excellent Gooch method (summarised below), of separation by amyl alcohol, is to be followed, after removal of the

* Preferred to platinum because of the possibility, under certain rare and ill-understood conditions, of the formation of an insoluble sub-chloride of platinum, probably by reaction between the platinum of the dish and that of the salt. (See also Bohn, *Zeit. fur Anal. Chemie*, 1899, vol. xxxviii., p. 349).

† Precht (*Zeit fur Anal. Chemie*, 1879, vol xviii., p. 513), claims that this is to be preferred to 80 per cent alcohol, especially if evaporation has been carried to dehydration of the sodium salt. Atterberg disputes this final statement, and says that 80 per cent alcohol gives better results.

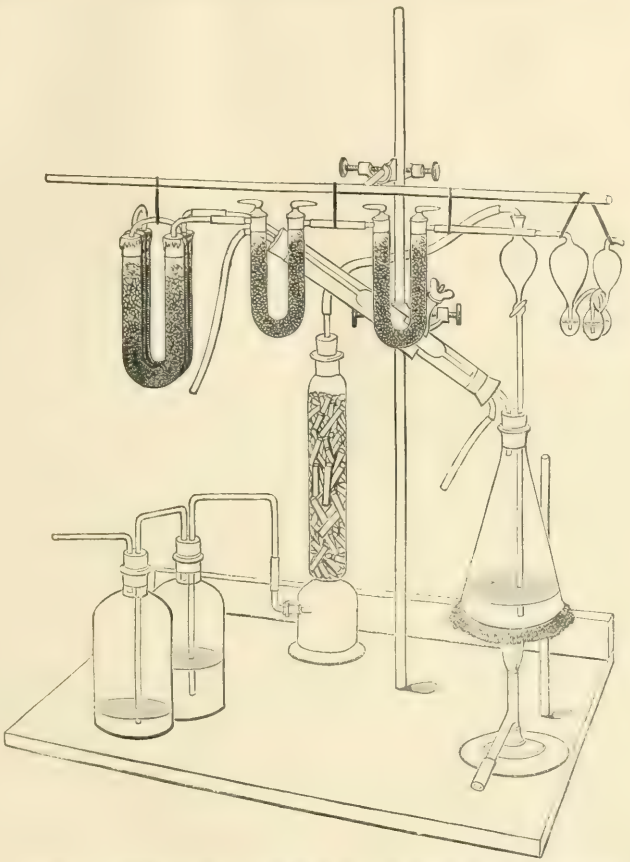


Fig. 15.—Compact Form of Apparatus for Estimation of Carbon Dioxide.

platinum by hydrogen gas.* In rock analysis there need be no fear of enough lithium falling with the potassium to cause any concern.

If ammonium carbonate alone has been relied on to separate all calcium (see above), the few tenths of a milligrm. of calcium chloride that escaped precipitation can now be found with the sodium.

* When haste is not an object, this way of Bunsen's for removing platinum from the chlorides of the alkalis is by far the neatest and most satisfactory. The small flask containing the solution is placed in a water-bath and attached to a hydrogen generator. After expelling all air the flask is closed, without breaking connection with the generator, and left to itself, except for occasional light shaking up, till reduction is accomplished. A more expeditious and very satisfactory reduction is effected by evaporating the solution to dryness with metallic mercury, then heating to expulsion of the excess of mercury and of its chloride (Sonstadt, *Journ. Chem. Soc.*, 1895, vol. lxvii., p. 984), who thus reduce potassium-platinic chloride in order to weigh its platinum.

Gooch's Method for Separating Lithium.*

To the concentrated solution of the chlorides amyl alcohol is added, and heat is applied, gently at first, to avoid danger of bumping, until, the water disappearing from solution, and the point of ebullition rising and becoming constant for some minutes at a temperature which is approximately that at which the alcohol boils by itself, the chlorides of sodium and potassium are deposited and lithium chloride is dehydrated and taken into solution. At this stage in the operation the liquid is cooled, and a drop or two of strong hydrochloric acid added to reconvert traces of lithium hydrate in the deposit, and the boiling continued until the alcohol is again free from water. If the amount of lithium chloride present is

* *Proc. Amer. Acad. Arts Sci.*, 1886, p. 177; *Bull. U.S Geol. Survey*, 18-7, No 42, p. 73; Chemical News, 1887, vol. lv., pp. 18, 29, 40, 56, 78; *Amer. Chem. Journ.*, 1887, vol. ix., p. 33.

small, it will now be found in solution, and the chlorides of sodium and potassium will be in the residue, excepting the traces for which correction will be made subsequently. If, however, the weight of lithium chloride present exceeds 10 or 20 milligrms., it is advisable at this point, though not absolutely essential to the attainment of fairly correct results, to decant the liquid from the residue, wash the latter a little with anhydrous amyl alcohol, dissolve in a few drops of water, and repeat the separation by boiling again in amyl alcohol. For washing, amyl alcohol, previously dehydrated by boiling, is to be used, and the filtrates are to be measured apart from the washings. In filtering it is best to make use of the perforated crucible and asbestos felt, and apply gentle pressure. The crucible and residue are ready for the balance after drying for a few minutes directly over a flame turned low. The weight of insoluble chlorides actually obtained in this manner is to be corrected by the addition of 0·00041 grm. for every 10 c.m.³ of amyl alcohol in the filtrate, exclusive of washings, if the insoluble salt is entirely sodium chloride, 0·00051 grm. for every 10 c.m.³ if potassium chloride constitutes the residue, and if both sodium and potassium chlorides are present, 0·00092 grm.; but . . . the entire correction may in any case be kept within very narrow limits if due care be given to the reduction of the volume of residual alcohol before filtration. The filtrate and washings are evaporated to dryness, treated with sulphuric acid, the excess of the latter driven off, and the residue ignited to fusion, and weighed. From the weight thus found the subtraction of 0·00050 grm. is to be made if sodium chloride constitutes the precipitate, 0·00059 grm. if potassium chloride alone is present in the residue, and 0·00109 grm. if both these chlorides are present, for every 10 c.m.³ of filtrate, exclusive of washings.

Amyl alcohol is not costly, the manipulations of the process are easy, and the only objectionable feature—the development of the fumes of amyl alcohol—is one which is insignificant when good ventilation is available.

The process has been used for some months frequently and successfully, by others as well as by myself, for the estimation of lithium in waters and minerals.

Separation of Alkalis by other Methods.

When, as may happen in rare instances, it is necessary to estimate alkalis in the main portion after the elimination of silica, alumina, lime, &c., in one of the usual ways, the question of a suitable method for separating magnesium becomes important.

The Mercuric Oxide Method.—The old barium-hydroxide method is not to be recommended. The mercuric oxide method of Zimmermann, whereby the magnesia is precipitated, from solution of the chlorides by moist, freshly precipitated, and alkali-free mercuric oxide, can give satisfactory results. The oxide is added in excess to the solution in a platinum crucible, and evaporated to dryness. Then the mercuric chloride and most or all of the excess of oxide are expelled by cautious heating. On leaching with water the magnesia remains on the filter. With more than 1 per cent of magnesia the operation must be repeated (Dittrich).

The Ammonium Carbonate Method.—Lately the once favoured method of precipitating the magnesium by neutral ammonium carbonate in concentrated solution has been again recommended.* The magnesium solution must be as strongly concentrated as possible, and a great excess of ammonium carbonate solution must be used. A voluminous precipitate forms, which dissolves on vigorous stirring if enough of the precipitant was used. After a time a crystalline precipitate falls—a double carbonate of magnesium and ammonium—which is insoluble in a concentrated solution of ammonium carbonate. Allow to stand for six to twenty-four hours. Wash with the concentrated ammonium carbonate solution. It is probably no exercise of undue caution to re-dissolve and re-precipitate, to make sure of getting all alkali in the filtrate.

The Amyl Alcohol Method.—Under certain circumstances, notably absence of lithium, the method of Gooch developed by Riggs (*Am. Journ. Sci.*, 1892, Third Series, vol. xliv., p. 103), may be satisfactory. It is similar to that of Gooch for separating lithium from sodium and potassium chlorides by amyl alcohol, and involves the same solubility corrections for the alkali chlorides above noted in the description of Gooch's method. Riggs's summary is as follows:—

Evaporate the solution nearly or quite to dryness. Dissolve the residue in as little water as possible, and add a few drops of hydrochloric acid. Then add 30—40 c.c. of amyl alcohol, and expel the water by bringing the alcohol to boiling. Continue the boiling until the volume of the solution is reduced to 10 c.c., or even considerably less. In filtering, it is of great advantage to use a perforated crucible and an asbestos felt, and to filter under pressure. In case the total chlorides exceed 0·2 grm. it may be advisable to decant the liquid, wash the residue, re-dissolve, and repeat the precipitation. If this be not done, the precipitate should be re-dissolved with the least quantity of water, a few drops of hydrochloric acid added, and the precipitation repeated in the original solution. The filtrate is transferred to a weighed platinum dish and evaporated. Water is added before the alcohol has been expelled, and the evaporation continued. The residue is dissolved in water. Sulphuric acid is added in slight excess. This solution is evaporated to dryness, the residue ignited and weighed, and the treatment with sulphuric acid is repeated. The residue of insoluble chlorides may be transferred to the weighed perforated crucible, and dried at a temperature below their melting points, or it may be dissolved and the solution transferred to a weighed platinum dish, evaporated, and the residue dried as above and weighed.

As with the Gooch method for lithium, the numerous tests results are good.

XXI. *Carbon Dioxide, Carbon.*

For this estimation an apparatus (Fig. 15) permanently set up is used, of which several forms have been described by different writers. The rock powder is boiled with dilute hydrochloric acid in a small Erlenmeyer flask, attached to an upward-inclined condenser, whence, after passing through a compact arrangement of drying tubes—first, one of calcium chloride, then one of anhydrous copper sulphate to retain hydrogen sulphide from decomposable sulphides, and any hydrochloric acid that may pass over, and, finally, a second calcium chloride tube—the carbon dioxide is retained by absorption tubes filled with soda-lime followed by calcium chloride. Of course arrangement is made for a current of CO_2 free air with which to sweep out the apparatus before and after the experiment, and for a slow current during its continuance. The results are very accurate, and the determination can be quickly carried out.

In the preliminary qualitative test for carbon dioxide, it must be remembered that while calcite gives off its carbon dioxide on treatment with cold acid, dolomite and siderite do not, and hence warming should not be omitted; otherwise, a few tenths per cent of carbon dioxide can very well be overlooked. Moreover, the powder should first be stirred up with a little hot water, to remove all entangled air which might otherwise be mistaken for carbon dioxide.

It has been already shown under "Water" (p. 112) how, in case of need, the determination of carbon dioxide can be combined with that of water by fusion with lead chromate or potassium chromate. This latter method must always be resorted to when the carbon of graphite or carbonaceous matter has to be estimated. If carbonates are present at the same time the result of the test includes

* Wülfing, *Ber. Deutsch. Chem. Gesell.*, 1899, vol. xxxii., p. 2214. The neutral carbonate is prepared by dissolving 230 grms. of ammonium carbonate in 180 c.c. of ammonia of 0·92 specific gravity and enough water to make 1 litre.

the carbon from both sources, and a separate determination by the wet way of that of the carbonates is necessary.

XXII. *Chlorine.*

To make sure of getting all the chlorine, it is best to fuse with chlorine-free sodium-potassium carbonate, or even sodium carbonate alone, first over the full burner, then for a moment or two over the blast, leach with water, acidify with nitric acid, and precipitate by silver nitrate without preliminary separation of silica. If 1 grm. of material has been used no precipitation of silica need be feared on acidifying or on standing.

In many cases it is quite sufficient to attack the powder by chlorine-free hydrofluoric acid and a little nitric acid, with occasional stirring, and after filtering through paper fitted into a large platinum cone or rubber funnel, to throw down the chlorine by silver nitrate. The presence of nitric acid is necessary, since otherwise ferrous fluoride reduces silver nitrate with deposition of crystallised silver. When coagulated by heating and stirring, the precipitate is collected on the filter, washed, dissolved by a little ammonia, and re-precipitated by nitric acid, when it can be collected in a Gooch crucible and weighed, or, if very small in quantity, on a small paper filter, which is then dried, wound up in a tared platinum wire, and carefully ignited. The increased weight of the wire is due to the metallic silver of the chloride which has alloyed with it.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 2nd, 1901.

Prof. EMERSON REYNOLDS, F.R.S., President, in the Chair.

MESSRS. Storr and Talbot were formally admitted Fellows of the Society.

The following certificates were read for the first time:—Ormsby Gore Adams, Stawell, Victoria; Joseph Samuel Bridges, 45, Thistlewaite Road, Clapton, N.E.; Adolf Ludwig Ferdinand Lehmann, Bangalore, Mysore, India; William Lowson, 83, Kyrle Road, Clapham Common, S.W.; James Bertram Russell, 356, Padiham Road, Burnley; Thomas Sandford, 2, Market Place, Ulverston; Samuel Edward Sheppard, Ravensmere, Bromley Road, Catford, S.E.; Andrew Biggam Smith, Queenstown, Cape Colony; George William Gerald Tatam, Mercers' Hall, Cheapside, E.C.; James Whittle, 30, Bridge Street, Morpeth.

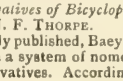
A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Messrs. William C. Anderson, M.A., D.Sc.; George Stanfield Blake; Edward Richards Bolton; Edward G. P. Bousfield; Percival J. Burgess, M.A.; William Carter; Ernest Clark, B.Sc.; Thomas Kennedy Cockburn; Eustace Coddington, B.A.; Walter Stevens Crocker; Henry Drysdale Dakin; Raymond Dubois, B.Sc.; William Henry Duckworth; Albert Ernest Dunstan, B.Sc.; Samuel Philip Eastick; Hugh Edward Ellis; John Vargas Eyre; John Hanley; John A. Harrison, B.Sc.; Francis R. Henley, B.A.; Henry Herbert Higgs, B.Sc.; Alfred James Hyder; William Henry C. Jemmett, B.A.; Ernest Alfred Lewis; Oscar Loewenthal; Alex. McKenzie, M.A., Ph.D., D.Sc.; Charles Edward Kenneth Mees; Albert John Murphy; Arthur Theodore Neil, B.A.; Edgar Neumann, B.A., Ph.D.; William Oldershaw; Arthur Peacock, B.Sc.; William Robertson; William Hammond Robinson, M.A.; William Shepperson; C. Edmund Shaw Sherratt; Samuel Slefrig, B.Sc.; Henry Ewing Smith; James Smith; Samuel Fenton Stell; William Henry Taylor; Herbert Ackerman Tozer, B.A.; Joseph De Verteuil; George Edward Welch, B.Sc.; Adam Storer Wylie.

Professor ARMSTRONG requested that the abstract of Professor Perkin's paper might be read, and suggested that it might be desirable to arrange for accounts to be given by persons specially selected of the work of authors who were unable to be present in person.

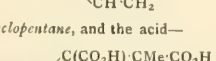
Of the following papers, those marked * were read:—

*74. "*The Synthetical Formation of Bridged Rings.* Part I. *Some Derivatives of Bicyclopentane.*" By W. H. PERKIN, jun., and J. F. THORPE.

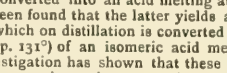
In a paper recently published, Baeyer (*Ber.*, 1901, xxxiii., 3771) has developed a system of nomenclature for bridged-rings and their derivatives. According to this system, the hydrocarbon—



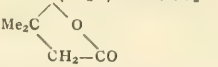
is named *bicyclopentane*, and the acid—



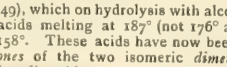
previously described (*Proc.*, 1900, xvi., 151)) is therefore *trimethylketobicyclopentanedicarboxylic acid.* It has already been stated that this acid, when digested with potash, is converted into an acid melting at 237°, and it has since been found that the latter yields an anhydride (m. p. 96°) which on distillation is converted into the anhydride (m. p. 131°) of an isomeric acid melting at 181°. Careful investigation has shown that these acids, which are evidently stereoisomeric, are not furfuran derivatives, as was at first supposed, but are *lactones* of *trimethylhydroxybutanetricarboxylic acid*—



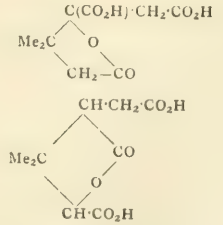
disruption of the whole bicyclopentane ring having taken place during their formation. A somewhat similar decomposition is shown by *ethyl dimethyldicarboxytrimethylenemalonate*—



(*loc. cit.*, p. 149), which on hydrolysis with alcoholic potash yields two acids melting at 187° (not 176° as previously stated) and 158°. These acids have now been shown to be the *lactones* of the two isomeric *dimethylhydroxybutanetricarboxylic acids*—

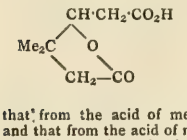


and—



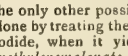
the trimethylene ring having been broken during hydrolysis; but unfortunately so far it has not been possible to decide which formula belongs to the former and which to the latter of the two acids.

Both acids on heating lose carbon dioxide, and are converted into the *lactones* of two isomeric *dimethylhydroxybutanedicarboxylic acids*, probably—



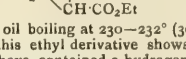
that from the acid of melting-point 187° melts at 108°, and that from the acid of melting-point 158° at 154°.

During the investigation of the bicyclopentane derivatives, it became necessary to prove conclusively that ethyl dimethyldicarboxytrimethylenemalonate really had the constitution assigned to it above, and that it was not a tetramethylene derivative of the formula—



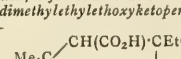
which was the only other possibility.

This was done by treating the ester with sodium ethylate and ethyl iodide, when it yielded *ethyl dimethylethyldicarboxytrimethylenemalonate*—

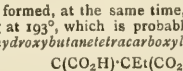


a colourless oil boiling at 230—232° (30 m.m.). The formation of this ethyl derivative shows that the original ester must have contained a hydrogen atom replaceable by sodium, and the tetramethylene formula given above is therefore excluded.

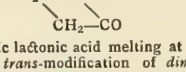
When this ethyl substitution product is digested with alcoholic potash, it yields a dibasic acid (m. p. 175°) which is probably *dimethylethylethoxyketopentamethylenedicarboxylic acid*—



and there is formed, at the same time, a tribasic lactonic acid melting at 193°, which is probably the *lactone* of *dimethylethylhydroxybutanetetracarboxylic acid*—



and a dibasic lactonic acid melting at 213°, which is probably the *trans*-modification of *dimethylethylhydroxybutanetricarboxylic acid*—



The corresponding *cis*-modification, which is obtained by the action of hydrochloric acid on the dimethylethyloxyketopentamethylenedicarboxylic acid mentioned above, melts at 144°, and gives an anhydride melting at 168°.

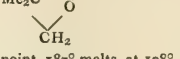
The ease with which disruption of the trimethylene ring takes place in the formation of these lactones is very remarkable; the only other similar case which is known is that described by Buchner and Witter (*Ber.*, 1894, xxvii., 871).

During the course of the investigation of the bicyclopentane derivatives, some interesting derivatives of *ββ-dimethyl glutaric acid*, $CO_2H{\cdot}CH_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H$, have been prepared and examined, and the results may be briefly summarised as follows:—

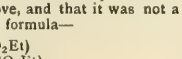
$\alpha\alpha_1$-Dibromodimethylglutaric acid—

$$CO_2H{\cdot}CHBr{\cdot}CMe_2{\cdot}CHBr{\cdot}CO_2H,$$

is obtained on treating dimethylglutaric anhydride with phosphorus pentachloride and bromine and digesting the product with anhydrous formic acid; it melts at 187—189°, and when treated with pyridine or boiled with water it yields the lactone of *α-bromo-α_1-hydroxydimethylglutaric acid*—



This melts at 169—170°, gives an ethyl ester boiling at 201° (45 m.m.), and is characterised by the great stability of its bromine atom, which is not removed even by boiling with silver nitrate and nitric acid. Strong potash, however, converts it into the *lactone* of *$\alpha\alpha_1$-dihydroxydimethyl glutaric acid*—



which melts at 142°.

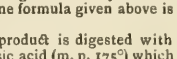
During the bromination of dimethylglutaric acid, a small quantity of *αα-dibromodimethylglutaric acid*—

$$CO_2H{\cdot}CBr_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H,$$

is formed, and this, on boiling with sodium carbonate, yields *αα-dihydroxydimethylglutaric acid*—

$$CO_2H{\cdot}C(OH)_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H,$$

which melts at 84° and behaves in many of its reactions as the keto-acid, $CO_2H{\cdot}CO{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H$, containing 1 molecule of water less. Thus it combines with *o*-toluylene diamine, and on reduction with sodium amalgam is converted into the lactone of *a-hydroxydimethylglutaric acid*—



which melts at 112°, and has already been described (*Trans.*, 1899, lxxv., 56).

*75. "*Lead Silicates in Relation to Pottery Manufacture.*" By T. E. Thorpe, C.B., F.R.S., and C. Simmonds, B.Sc.

As is well known, the use of oxides and basic carbonates of lead in glazes employed by potters is attended with danger to the health of the workpeople on account of the ready solubility of these compounds in the acids of the animal organism. Attention was drawn to the fact that lead silicates or boro-silicates, or complex silicates of lead and other metals, can be used instead of the oxides or carbonates as a means of introducing lead into the glaze. On the Continent this use of lead silicates is far more common than in England, and it is generally recognised that their employment has greatly tended to minimise the risk of lead-poisoning. This is due to the fact that the lead silicates used in the continental factories are of a high degree of insolubility so far as the lead is concerned.

On examining a number of lead silicates used or proposed for use in England, it was found that many were attacked by dilute acids practically to the same extent as the oxides or carbonates. That is, they yielded the whole, or nearly the whole, of their lead to the action of acids comparable with the acids found in the human system—such as, for example, the hydrochloric acid of the gastric juice. Other specimens were more resistant, but still yielded a large proportion of their lead. On the other hand, the specimens obtained from the Continent, as well as many which have recently been produced by English manufacturers, gave up only small quantities of lead when tested under the special conditions described.

A large number of specimens was therefore analysed in order to ascertain, if possible, to what variations in chemical composition these differences of behaviour were due.

The condition on which the insolubility of the lead depends was found to be, primarily, the existence of a certain ratio between the whole of the base-oxides on the one hand, and the whole of the acid-oxides on the other. This becomes eventually referable to the hypothetical silicic acids from which the silicates may be considered to be derived. For working purposes, the relation may be more simply expressed as—

sum of percentages of base-oxides, expressed as PbO
sum of percentages of acid-oxides, expressed as SiO_2'

or, alternatively, as—

number of acid molecules
number of base molecules'

the latter ratio being obtained by dividing the percentage of each oxide by its molecular weight, and then dividing the sum of the quotients for the acid-oxides by the sum of the quotients for the base-oxides.

Provided the ratio falls within certain definite limits, the amount of lead extracted under the prescribed conditions is always small. It does not depend upon the quantity of lead in the silicate, which may have any value up to 50 or 55 per cent. The other bases usually present (lime, alumina, and alkalis) may also vary considerably, replacing one another, and also the lead oxide, within very wide limits without prejudice to the insolubility of the lead.

Analyses and formulæ of a number of silicates were given, together with tables showing the dependence of the solubility of the lead in the silicates upon the ratios mentioned above.

Discussion.

Mr. F. J. Lloyd asked whether experiments had been made using smaller quantities of solution than 1000 parts to 1 part of substance. The acid present in 1000 c.c. would be about seven times as much as that required to dissolve 1 grm. of lead oxide. The conditions which influenced the solubility of substances in dilute acid solutions were of especial interest to agricultural chemists. He had found in some experiments that the volume of solution employed appeared to materially affect the solubility, and wished to know whether the authors had had a similar experience during their investigation.

Prof. Tilden enquired whether the authors had paid special attention to the degree of fineness of the powders submitted to the action of the acid. Some facts had already been published which seemed to show that the apparent solubility of a frit was seriously influenced by the amount of trituration to which the substance had been subjected before bringing it into contact with the acid.

Prof. Clowes said it would be of interest to know if the solvent action of acids other than hydrochloric acid had been tried, and with what results. He also asked whether the method of testing finished articles purporting to be covered with leadless glaze, by exposing them to the action of dilute hydrochloric acid for some time, and examining the solution for the presence of lead, was satisfactory, and what were the best conditions for applying such a test.

Mr. Elworthy asked whether the authors had estimated the solubility of the frits or glazes in salt solutions, as they were much more likely to come into contact with salt solution than with free hydrochloric acid, especially during the preparation of food, and whether the lead dissolved from the frit existed in the solution as chloride or as a soluble silicate.

Prof. Carmody asked whether any comparisons had been made between the amount of lead oxide soluble in the frits before and after their application.

Mr. Simmonds, in reply, stated that an excess of acid was necessary, for otherwise misleading results were obtained; this was due to the curious fact that certain kinds of lead silicate reacted with a neutral solution of lead chloride, and removed the lead from solution, probably as an insoluble oxychloride. The volume of acid selected must be sufficiently great to ensure that there should be no very considerable weakening of its strength by the action of the various acid-neutralising constituents, of which, it should be borne in mind, there might be several besides the lead.

As regards fineness of subdivision, some of the specimens were sent ready ground, and were stated by the manufacturers to be in the condition in which they were to be used for glazing pottery ware; these were tested as received. The other specimens were ground to an impalpable powder in an agate mortar. Various solvents had been experimented with—for example, lactic and acetic acids—but the results threw no greater light on the subject than those obtained with hydrochloric acid; consequently, the experiments were not persisted in. Salt solution had not been tried. He did not know whether testing the glaze on table ware with hydrochloric acid had been suggested, but in Germany there was a provision that such ware should not give up lead when boiled for half an hour with 4 per cent acetic acid.

With reference to the state in which the lead existed when dissolved from a silicate, whether as a lead silicate or as a lead chloride, complete analyses of several of the solutions had been made, and some small quantity of silica was always present. The lead, or a part of it, may therefore, perhaps, have dissolved as a basic silicate.

76. "*The Preparation and Properties of* 2 : 6-*Dibromo-*4-*nitrosophenol.*" By M. O. Forster and W. Robertson.

2 : 6-Dibromo-4-nitrosophenol is produced by the action of potassium hypobromite on *p*-nitrosophenol dissolved in potassium hydroxide solution (compare Fischer and Hepp, *Ber.*, 1888, xxi., 674); the *potassium*, *acetyl*, and *benzoyl* derivatives are well defined. Dilute nitric acid oxidises the substance to 2 : 6-dibromo-4-nitrophenol, but the concentrated acid converts it into 2-bromo-4 : 6-dinitrophenol. Tin and hydrochloric acid reduce 2 : 6-dibromo-4-nitrosophenol to 2 : 6-dibromo-4-aminophenol, of which the *benzoyl* derivative is well defined.

77. "*The Chlorination of Toluene.*" By W. P. Wynne.

In consequence of the publication of an abstract of a paper by Cohen and Dakin (*Proc.*, 1901, 91), the author wishes to state that he has been, and is, engaged in a study of the chloro-derivatives obtained in chlorinating toluene under Seelig's conditions (*Trans.*, 1892, lxi., 1051). The six dichlorotoluenes, and their sulphonic acids, chlorides, and amides, to which Cohen and Dakin refer, were prepared and examined in this connection (*loc. cit.*, p. 1042; Wynne and Greeves, *Proc.*, 1895, xi., 151). Moreover, the 2 : 5-dichlorotoluene, which these authors state is very probably formed in presence of the mercury-aluminium couple, has been recognised as present in considerable quantity in the mixture of dichlorotoluenes obtained by Seelig's method.

PHYSICAL SOCIETY.

Ordinary Meeting, May 10th, 1901.

Prof. S. P. Thompson, President in the Chair.

A paper on "*Applications of Elastic Solids to Metrology*" was read by Dr. Chree.

The ordinary conception of a solid is apt to be that of a body whose shape and volume are variable only with temperature. Elastic changes in dimensions are necessarily small in most bodies of limited size, and they are often negligible even in exact work. The object of the present paper is to exemplify the bearing of elasticity on physical measurements. Many of the results depend ultimately on a previous paper by the author in which expressions were obtained for the mean strains, and for the change in total volume of any homogeneous elastic solid acted on by any given system of forces throughout its mass or over its surface. The formula is first applied to the case of a right circular cylinder, and it is shown that the action of gravity can be eliminated by taking for the length and volume the means of the results obtained when the cylinder is suspended by a string, and when it stands upon its base on a flat surface. The effect of the pressure of a surrounding medium of constant density upon the shape and volume of an isotropic solid is considered, and the theory is extended to the case of an

œolotropic solid in a medium of varying density. If a standard kilogrm. of platinum-iridium were suspended instead of being supported on its base, the alteration in volume would be 66×10^{-8} c.c., and if it were transferred from air at atmospheric pressure to a vacuum the alteration would be 24×10^{-8} c.c. The change in volume of the material of the walls of a flask containing liquid is next investigated, and it is shown that the change is independent of the thickness of the walls, the mean expansion per unit of volume being inversely proportional to the whole volume. Whether the alteration consists of an increase or a decrease depends upon the dimensions of the vessel. Theoretically a flask whose inner surface is a cone of any solid angle, vertex downwards, would have the property that the volume of the material of its walls would be unaffected by the pressure of any liquid it might contain. We cannot in general determine the effect on the internal capacity of a vessel due to the pressure of contained liquid, but if the walls are coaxial right circular cylinders, the common axis being vertical, the solution is possible. The increase in volume per unit of volume inside a thin walled circular tube varies directly as the density of the liquid, the height of the mark, and the radius of the tube, while it varies inversely as the thickness of the walls. As a numerical example, a glass-tube 12·7 c.m. high, 10 c.m. internal diameter, and 1·5 m.m. thick, would hold 0·11 grm. more mercury than it would if inelastic. The solution is possible in the case of a spherical shell, and this problem is also investigated in the paper. The author next considers the application of the theory of elasticity to standards of length, and to give a more exact idea of the problems actually occurring in metrology he deals particularly with five forms:—The standard yard, the international prototype metre of × section, a working standard belonging to the Bureau International, and two deflection bars used in magnetometers. The shapes of these bars are devised partly with the object of facilitating equalisation of temperature throughout the bar. Most modern standards are supported not over the whole lower surface, but either on two symmetrical rollers or on three points. An exact solution of the elastic problem presented by a heavy bar supported on points or rollers has not yet been obtained, but the Bernoulli-Euler solution is very accurate except near the supports. In using standards of length it is the horizontal projection of the graduated surface that usually concerns us, and it is proved that unless we deal with a very long bar the difference between the chord and the arc is very small. This difference increases as the supports are moved outwards, from their most favourable position, towards the end of the bar. The standard yard in this respect compares unfavourably with more modern types. The curvatures and lengths of bars supported in various ways, both loaded and unloaded, are treated at length, and it is shown that by a proper arrangement of supports the alteration in length between two points due to bending can be rendered so small as to be of no practical importance. In the metre prototypes of × section the divisions occur on the neutral surface, and their distance apart is unaffected by stretching of the material. In the case of magnetometer deflection bars it is advisable to have the magnet as near to the bar as possible. Increasing the distance between them is equivalent to having the scale a long way from the neutral surface. Increasing the weight of the magnet and carriage, or decreasing the distance between the two points of support by reducing the size of the graduated circle, produce errors on account of bending.

Prof. Everett congratulated the author upon the practical application of a difficult theory to the measurements of lengths and volumes.

Mr. Watson said that it was usual in deducing the radius of a coil from the measurement of its circumference with a steel tape to diminish the result by half the thickness of the tape. He would like to know if this was the right correction to apply. In measuring the circumference of a cylinder it is necessary to wind the tape in a spiral so as to bring the divisions side by side. This gives a result which is too great and not too small, as might at first sight be imagined.

Mr. Campbell asked if any special experiments had been performed to determine directly the bending of standards at different points of their length.

Dr. Lehfeldt asked if the work of the author could be used to determine the pressure corrections of thermometers. He would like to ask why it was necessary to use supports instead of allowing a standard to rest on a flat surface.

The Chairman said that the paper was important because of its bearing on the question of the relation between the units of different nations. He drew attention to the alteration of the factor converting metres into inches, and asked if it was due to alterations in the properties of matter or to errors of observation. The two legal definitions of the gallon differ by an appreciable amount, and it would be interesting to know if this discrepancy could be due to changes in the volume of measures due to the liquids contained by them.

Dr. Chree, in reply to Mr. Watson, said the correction would depend upon the diameter measured, because that determined the curvature of the tape, and therefore the stretching produced. In reply to Mr. Campbell the author stated that experiments had been made upon the bending of bars, and they agreed well with theory. The correction formula obtained for a thermometer is similar to the ordinary one used. A bar is usually supported so as to remove the uncertainty of the distribution of surface pressure when it rests on a flat surface, not a true plane. In reply to the President, Dr. Chree said that the alteration of the factor converting metres into inches was probably due to errors of observation on account of the width of the divisions of the standard yard, and on account of the difficulty of obtaining the bar at the standard temperature of 62° F.

A paper, by J. Rose-Innes and Prof. S. Young, on "*The Thermal Properties of Isopentane compared with those of Normal Pentane*" was read by Mr. Rose-Innes.

In previous papers the authors have investigated experimentally the thermal properties of isopentane and normal pentane, and have stated certain conclusions from their observations. The present paper gives the conclusions reached after a more exhaustive examination of the experimental results of the former papers. The quantity $RT - pv$ at any volume and temperature is called the departure from Boyle's law at that point, and it is found that there is a constant ratio between the departures from Boyle's law of isopentane and normal pentane at the same volume and temperature. To test the law, a probable value of the ratio was determined, and by means of it a large number of values of pv for isopentane were calculated from results for normal pentane. These calculated values fall upon the same curve as the observed values, and agree with them to within about 1 per cent. The authors are confirmed in their previous conclusion, that the difference of pressure between two isomeric substances at the same temperature and volume involves the same power of the density as the first deviation from Boyle's law, *i.e.*, the second power.

Mr. J. M. Gray said the numbers obtained would be valuable to him, and he would make use of them in his calculations. He was sorry, however, that the authors had dealt with empirical formulæ instead of rational formulæ deducible from the theory of gases.

Dr. Chree asked how the temperatures were measured.

Mr. Rose-Innes said recourse had been had to empirical formulæ because they found theoretical formulæ useless. He gave examples of the failure of well-known equations to satisfy experimental results. The temperatures were measured with a constant volume air thermometer, a small correction—less than the errors of experiment—being employed to reduce the readings to the thermodynamic scale.

The Society then adjourned until May 31st.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxii., No. 16, April 22, 1901.

Estimation of Nitric Acid in Natural Waters by means of Stannous Chloride.—H. Henriet.—An acid solution of stannous chloride is known to transform nitric acid into hydroxylamine if the stannous chloride is present in excess and if there is enough water present to prevent the hydrochloric and nitric acids from reacting upon one another. The author investigates this reaction, and finds that, at boiling-point, the nitric acid is transformed quantitatively into hydroxylamine; the reaction apparently taking place according to the following equation:—

$$3SnCl_2+NO_3K+8HCl=$$
$$=3SnCl_4+NH_2OHHCl+KCl+2H_2O.$$

This reaction can be utilised for the estimation of the nitrates, if an iodine solution is used for the estimation of the excess of stannous chloride, $SnCl_2+2I+4HCl=SnCl_4+2HI$. From these equations, it will be seen that six atoms of iodine correspond to one atom of nitrogen.

Action of various Alcohols on some Acetals of Monovalent Alcohols.—Marcel Delépine.—If methylal is heated with amyl alcohol or diamylic formal with methyl alcohol the same products result, a distillation of the mixture resulting in methylal, methyl alcohol, amylic alcohol of mixed formal (resulting from a partial substitution), and diamylic formal. The reactions may be represented by the following equations:—

$$CH_2(OCH_3)_2+2C_5H_{11}OH\rightleftarrows CH_2(OC_5H_{11})_2+2CH_3OH\ ;$$
$$CH_2(OCH_3)_2+C_5H_{11}OH\rightleftarrows CH_2(OCH_3)(OC_5H_{11})+CH_3OH\ ;$$
$$CH_2(OC_5H_{11})_2+CH_3OH\rightleftarrows CH_2(OCH_3)(OC_5H_{11})+C_5H_{11}OH.$$

A similar reaction occurs when ethyl alcohol reacts with diamyl formal, methyl alcohol with dipropyl formal, and propylic alcohol with methylal. Five substances are produced which are very difficult to separate.

Three New Alkaloids from Tobacco.—A. Piçet and A. Rotschy.—By submitting the nicotine obtained from tobacco to a series of fractional distillations, two well-defined fractions are obtained: one boiling at 256—268°; and the other, smaller fraction, boiling at between 300° and 310°. This latter solidifies partially on cooling. The first fraction contains a liquid alkaloid of formula $C_{10}H_{12}N_2$, and has been given the name nicoteine. The solid alkaloid, after crystallisation from dilute alcohol, can be obtained in little prismatic needles melting at 147—148°; this has been called nicotelline, and it apparently corresponds to the formula $C_{10}H_8N_2$. A third alkaloid is found in crude nicotine. By treating the nicotine with nitrous acid and distilling the product *in vacuo*, a small quantity of an oily nitrosamine is obtained, from which the base can be produced by boiling with hydrochloric acid; for this the name of nicotimine was adopted. This latter substance is an isomer of nicotine. The proportion of the new alkaloids in tobacco is very small as compared with nicotine; it can be approximately expressed as follows:—Nicotine, 1000; nicoteine, 20; nicotimine, 5; nicotelline, 1.

Action of Phenylhydrazine and Hydrazine on the two Isomeric Methylbutyrylacetylacetates. — M. Bongert.—The author describes the results obtained when hydrazine and phenylhydrazine react on the two isomers of methylbutyrylacetylacetate, and the preparation of a new body having the empirical formula $C_{12}H_{13}N_2O$. This latter differs from the corresponding pyrazolone by a single atom of hydrogen. This fact seems to indicate that the formula should be doubled, and that the substance is a bispyrazolone. This assumption has been verified.

Paraoxyhydratropic Acid.—J. Bougault.—This paper describes the properties and preparation of paraoxyhydratropic acid, $OH—C_6H_4—CH<^{CO_2H}_{CH_3}$.

New Reactions of Cyano-metallic Derivatives. (III.). Non-substituted β-Ketonic Ethers. — E. E. Blaise.—By the method described in a previous paper, the author prepares ethyl propionylacetate and ethyl butyrylacetate. The first of these bodies being separated from the products of the reaction by means of sodium bisulphite, and the second by transformation into the magnesium derivative.

A New derived Base from Glucose.—L. Maquenne and E. Roux.—The authors obtained, starting from the aldose oximes $C_nH_{2n}O_n$, a whole series of primary bases of the form $C_nH_{n+2}(OH)_{n-1}(NH_2)$. These are practically distinguished by their great stability and the absence of any action on cupro-potassium solutions. The authors also describe the base derived from ordinary glucose, which is in some measure the type of this new class of compounds, and which they designate by the name of glucamine.

Action of Alcoylcyanacetic Ethers on Diazoic Chlorides.—G. Favrel.—This paper gives an account of the action of alcoylcyanacetic ether on the chloride of diazobenzene, diazoparatoluene, and diazo-orthotoluene.

Reduction of Nitrated Azo-colouring Matters.—A. Rosenstiehl.—When nitramine is set free in a sulphonated azo-combination, it is much more soluble than when it is in a free state. This fact facilitates all reactions of reducing agents where the action takes place only on the nitramine, without the intervention of sulphonaphthol.

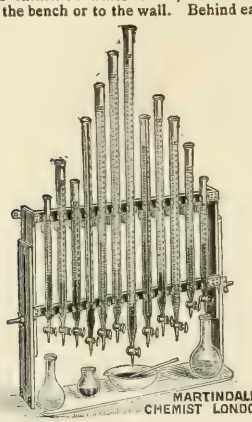
Two New Acetylenic Acids. Synthesis of Caprylic and Pelargonic Acids.—Ch. Moureu and R. Delange.—The authors prepare two new acetylenic acids and some of their immediate derivatives. Each of these acids, hydrogenated by sodium and boiling absolute alcohol, is converted into the corresponding saturated fatty acid—a transformation which allows of a new synthesis of two natural acids, caprylic and pelargonic acids.

MISCELLANEOUS.

Tannoform in Veterinary Practice.—Tannoform was first prepared by Merck about six years ago. It is the condensation product of tannic acid and formic aldehyde, and possesses simultaneously both the astringent action of the former and the antiseptic properties of the latter. Its composition corresponds to the formula $CH_2<^{C_{14}H_9O_9}_{C_{14}H_9O_9}$. In appearance it is a light, reddish-white, odourless, and almost tasteless powder, insoluble in water, but soluble in alcohol. Owing to the specific anhydrodic action of tannoform it was at first employed as a remedy against excessive perspiration of the feet, hands, and other parts of the body, and met with a hearty welcome from tourists, military, and sporting men. It is absolutely non-poisonous, and is tolerated in large doses without objection; it checks secretion, and destroys bacteria. Tannoform can be employed internally as a very active intestinal astringent, and has been found most effective in a large number of cases of intestinal catarrh. Very remarkable cures of infectious diarrhœas in young cattle are reported. Its applications to cuts and sores has given very good results owing to its antiseptic action, and it has been welcomed by veterinary surgeons as a valuable adjunct to their medicaments.

Tin Solder.—A useful form of tin solder has been placed upon the market by the Patent Solder Co , Limited, of 47, Old Street, E.C. The novelty consists in the rods of solder being "cored" with resin ; they are made in various sizes, from the thickness of a lead pencil downwards, and are very convenient to use. For little odd jobs in the laboratory its employment is a luxury, and if the price is reasonable this form of solder is likely to come into general use in the workshop, especially in the electrical trades.

New Burette Stand.—We have received from Mr. W. Martindale, of 10, Cavendish Street, W., a "common-sense" burette stand; the sketch shows the apparatus filled with tubes, and sufficiently explains the design. It is made in varnished white wood, and can either be screwed to the bench or to the wall. Behind each tube is



a little hook to hold a small bone memorandum tablet. Where titrations have to be frequently made it will be found very convenient; it also makes a useful store for burettes when not in use, as it takes up little room, and being fixed cannot get upset. The stand is made in two sizes to take six or twelve burettes.

The Higher Peroxides of Hydrogen.—A. Bach.—The author has already shown (*Comptes Rendus*, vol. cxxiv., p. 951), that the products of the oxidation of nascent hydrogen derived from hydride of palladium, oxidise a solution of indigo much more rapidly than does ordinary peroxide of hydrogen containing the same quantity of active oxygen. He was therefore obliged to admit the existence of peroxides of hydrogen more oxygenated than H_2O_2; to verify this he took a certain quantity of peroxide of hydrogen or other oxidising liquid, and simultaneously estimated its action on permanganate, and the volume of oxygen set free. The apparatus consists of a burette, a stoppered flask, a measuring tube, and a manometric tube, and is illustrated in the original paper; the flask and the measuring tube are kept immersed in water at a constant temperature. With peroxide of hydrogen, H_2O_2, the reaction is:—

$$5H_2O_2+2MnO_4K+3SO_4H_2 = 5O_2+SO_4K_2+2SO_4Mn+8H_2O.$$

But if the peroxide of hydrogen was H_2O_4, corresponding to K_2O_4, the reaction would give a double volume of oxygen (changing $5H_2O_2$ into $5H_2O_4$, and $5O_2$ into $10O_2$). Operating comparatively with commercial peroxide of hydrogen, the author has examined successively the products of oxidation of nascent hydrogen from palladium, peroxide of hydrogen obtained from dilute acids at very low temperatures, of tetroxide of potassium, and binoxide of sodium, and of "Caro's acid" (a mixture of concentrated SO_4H_2 with persulphate of potassium or even with H_2O_2). He arrived at the following results with regard to the oxygen liberated, taking that given off by ordinary peroxide of hydrogen as unity, for equal weights of $KMnO_4$ reduced:—

Ordinary peroxide of hydrogen from BaO_2 ..	1·00
Products of oxidation of nascent hydrogen ..	1·07
Peroxide of hydrogen from Na_2O_2	1·17
" " " K_2O_4	1·28
"Caro's acid"	1·65

M. Bach acknowledges that this increase of the oxygen set at liberty arises from the presence of *tetroxide of hydrogen*, H_2O_4; that is HO.O.O.OH, corresponding to the tetroxide of potassium. The trioxide, H_2O_3, does not appear to have any oxidising power.—*Berichte*, vol. xxxiii., p. 1506.

NOTES AND QUERIES.

Lactic Acid.—Could any of your reader give any information as to the "lactic acid" which is now becoming so largely used in tanning, and also to some extent in dyeing. Someone has informed the enquirer that it is obtained directly from potatoes through the action of some bacillus.—A Very Old Reader.

MEETINGS FOR THE WEEK.

Tuesday, 21st.—Royal Institution, 3. "On Cellular Physiology, with special reference to Enzymes and Ferments," by Allan Macfadyen, M.D., B.Sc.
—— Society of Arts, 8. "The Rise and Development of Egyptian Art," by Prof. W. M. Flinders Petrie, D.C.L.
Wednesday, 22nd.—Society of Arts, 8. "Testing and Training Distant Vision, with Special Reference to Military Requirements," by R. Brudenell Carter, F.R.C.S.
Thursday, 23rd.—Royal Institution, 3. "The Chemistry of Carbon," by Prof. Dewar, F.R.S., &c.
Friday, 24th.—Royal Institution, 9. "The Aims of the National Physical Laboratory," by Richard T. Glazebrook, M.A., D.Sc., F.R.S.
Saturday, 25th.—Royal Institution, 3. "The Rise of Civilisation in Egypt," by Prof. W. M. Flinders Petrie, D.C.L.

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AMMONIUM BROMIDE AND THE ATOMIC WEIGHT OF NITROGEN.*

By ALEXANDER SCOTT.

Although the whole of the recent work on the ratio of the atomic weights of hydrogen and oxygen relatively to one another seems to establish that ratio as 1 : 15·88 or 1·0075 : 16, I thought it would be not only of great interest, but of the highest importance if this ratio could be determined in some manner totally different from any that had been previously attempted, and depending in no way on determinations of the composition of water.

The ideal method was to find some atom or group of atoms which unites with hydrogen and with oxygen to produce compounds of sufficient stability for their equivalent weights to be accurately determined. We seem to have this in the three bases—hydrazine, ammonia, and hydroxylamine, which for this purpose may be regarded as having the formulæ NH_2, NH_3, NH_3O, hydrazine having one hydrogen atom less, and hydroxylamine one oxygen atom more than ammonia.

The hydrobromides of these bases seem from their general properties admirably adapted for comparison with one another by determining in each case the equivalent amount of pure silver.

Although the preparation and purification of the substances and the necessary careful study of their adaptability for the end in view has occupied rather more than two years, it was not anticipitated that any serious difficulty would occur in the case of the central member of the group, ammonium bromide. Nevertheless, such is the case, and the explanation of the discrepancies which exist between the classical work of Stas and my own is by no means easy.

Stas (*Œuvres*, i., 812), gives the ratio of ammonium bromide to silver as 98·032 : 107·93, whereas I find only 97·995 : 107·93; the corresponding values for ammonium are 18·077 and 18·040, and for the atomic weight of nitrogen 14·047 and 14·010.

Stas deduced the value above stated from seven experiments on samples of ammonium bromide prepared in different ways and apparently always against the same sample of silver.

He states (*Œuvres*, i., 790) :—"On le sait, le bromure d'ammonium peut être volatilisé sans décomposition dans un courant de gaz ammoniac sec. Dans le but de me procurer ce sel à l'état compacte et partant facile à peser et à manier, j'ai essayé d'avoir recours à cette volatilisation, mais après plusieurs tentatives infructueuses, j'ai été obligé d'y renoncer. En effet, à une température très-peu supérieure à sa volatilisation, il se dissocie, du brome même devient parfois libre. On constate aisément la présence de ce corps par la coloration de la vapeur du bromure, et *par la coloration en jaune du sel condensé*, qui a produit des fumées lorsqu'on l'a chauffé dans de l'ammoniaque seche."

The italics are those of Stas himself. He further remarks that his bromide, which was brilliantly white, and remained so indefinitely at the ordinary temperature under a bell-jar over potash, lost its whiteness, and became greyish (*grisâtre*) when heated in air at temperatures above 100°, that this greyness increased as the salt was heated from 115° to 180°, and that the whiteness was only partially restored by heating it in a current of ammonia.

All my samples were also brilliantly white, and showed no greyness when heated in air to 180°, although they lost their sparkling whiteness; this was due, however, to a change in the surface of the crystals owing to the slight sublimation which takes place when the salt, imperfectly dried, is heated to that temperature. No difficulty was experienced in subliming the salt either in a vacuum, in a mixture of ammonia and hydrogen, or in pure ammonia itself, and no trace of yellow colouration was observed in any instance, the condensed salt being a somewhat horny, translucent mass.

The silver employed was prepared from the pure silver of commerce by dissolving it in nitric acid, evaporating the solution to dryness, and fusing the salt for twenty minutes; the fused mass was then dissolved in water, filtered, and kept gently boiling for several hours with 10 to 15 grms. of freshly precipitated silver oxide, the oxides of lead, copper, and iron being thus precipitated and apparently completely removed.

After filtration, the solution of silver nitrate thus purified was added in small quantities at a time to a solution of equivalent quantities of ammonium formate and acetate sufficient to reduce rather more than the total silver nitrate added. The solution of ammonium formate and acetate was made by distilling pure formic and pure acetic acids into a solution of ammonia (which had been prepared by passing well washed ammonia into pure redistilled water in a porcelain beaker), until the solution was strongly acid; everything of a nature not very easily volatile was thus completely excluded from the reducing agent. It was suitably diluted and raised to the boiling-point in a flask of special non-attackable glass, and the silver nitrate solution added. The reaction which takes place is :—

$$HCO_2NH_4 + 2AgNO_3 = NH_4NO_3 + HNO_3 + 2Ag + CO_2$$

and

$$CH_3.CO_2NH_4 + HNO_3 = NH_4NO_3 + CH_3.CO_2H,$$

the use of the ammonium acetate being merely to exchange the liberated nitric for acetic acid. After being thoroughly washed and dried, the silver was fused with a little pure sodium and potassium carbonates along with a little nitre, granulated, and the above process repeated, the re-precipitated and thoroughly washed silver being raised to a low red heat in a muffle, and kept in the easily divided form thus obtained. Only 2 or 3 milligrms. of ferric oxide were separated by the second treatment from a kilogrm. of silver.

This silver was notably better than a sample prepared with the utmost care by the cuprous ammonium sulphite method so much employed for the purification of silver.

The hydrobromic acid employed was made in two ways: —(1). By distilling potassium bromide with somewhat diluted sulphuric acid, and frequent re-distillation (Squibb's process), and (2) by the reduction of bromine to hydrobromic acid by means of sulphurous acid, as I have described (*Trans.*, 1900, lxxvii., 649).

The ammonia was also from two sources :—(1). From ammonium sulphate drastically treated with nitric and sulphuric acids, and (2) from potassium nitrite reduced by means of zinc which had been fused with lead oxide. In both cases, all the precautions given by Stas were rigorously adhered to, and in some cases even exceeded.

The balance chiefly employed in the weighings was an excellent one by Bunge, and the weights were of platinum-iridium made by Messrs. Johnson, Matthey, and Co., and adjusted with great accuracy by Oertling.

The silver, after being heated over a spirit burner in pure hydrogen and weighed, was dissolved in a carefully stoppered bottle in pure nitric acid (sp. gr. 1·42), the bottle standing on the water-bath for an hour. After complete cooling, the pressure inside the bottle was almost always considerably less than that of the atmosphere, so that water could be drawn in when the stopper was carefully removed, and all possible loss of silver thus avoided.

The silver nitrate solution was then diluted and kept on the water-bath until both the solution and the atmosphere above it were quite colourless.

* From the *Transactions of the Chemical Society*, 1901, lxxix., p. 147.

The ammonium bromide, heated in almost every case to 180° for some hours in a current of hydrogen which had been bubbled through pure ammonia solution, and dried by passing over solid soda and metallic sodium, was weighed after being cooled in a vacuum, then dissolved and added to the silver solution in a room lit with red light only, the whole vigorously shaken, and this shaking frequently repeated. The excess of silver or bromide remaining in solution was determined (usually after two days) by means of standard solutions (which were in all cases weighed).

In the following summary all the weights given are reduced to vacuum weighings, and corrected for all errors in the face values of the weights. The atomic weight of silver is taken as 107·93.

To test the effect of sublimation on the salt, the third crop of crystals obtained by evaporating to dryness the mother-liquors from the ammonium bromide used in series IV. and V. below was employed. Obtained in this way, it was likely to be abnormally acid, and therefore would tend to give a low equivalent.

(*a*). Not sublimed, dried in hydrogen and ammonia at 180°.

4·89631 NH_4Br = 5·39380 Ag ∴ NH_4Br = 97·975.

(*b*). Sublimed once in Sprengel vacuum, but not dried or treated further.

2·45925 NH_4Br = 2·70914 Ag ∴ NH_4Br = 97·972.

(*c*) Sublimed twice in Sprengel vacuum, and dried in hydrogen and ammonia at 180°.

3·29478 NH_4Br = 3·62928 Ag ∴ NH_4Br = 97·982.

(*d*) Sublimed in hydrogen and ammonia and heated in the same at 180° for some hours.

4·46957 NH_4Br = 4·92273 Ag ∴ NH_4Br = 97·994.

(*a*), (*b*), and (*c*) show by their low equivalents that they were distinctly acid, which acidity was only overcome by sublimation in a strongly ammoniacal atmosphere.

The other samples of ammonium bromide were crystallised from *alkaline* solutions. The solutions of the dried bromide, like those of Stas, were all strongly acid to litmus.

I. Ammonia from ammonium sulphate. Hydrobromic acid from potassium bromide. Silver reduced by formate.

(*a*). 4·20661 NH_4Br = 4·63303 Ag ∴ NH_4Br = 97·996.
(*b*). 4·23664 NH_4Br = 4·66644 Ag ∴ NH_4Br = 97·989.

II. Ammonia from potassium nitrite. Hydrobromic acid from potassium bromide. Silver reduced by formate.

(*a*). 4·31464 NH_4Br = 4·75175 Ag ∴ NH_4Br = 98 001.
(*b*). 6·19233 NH_4Br = 6·82047 Ag ∴ NH_4Br = 97·990.

III. Same ammonium bromide as in I. Silver reduced by cuprous ammonium sulphite.

8·77664 NH_4Br = 9·66788 Ag ∴ NH_4Br = 97·981.

This silver was found to contain 0·0018 grm. of ferric oxide, hence the true equivalent weights are—

8·77664 NH_4Br = 9·66608 Ag ∴ NH_4Br = 97 999.

IV. Ammonia from ammonium sulphate. Hydrobromic acid from pure bromine. *First* crop of crystals. Silver reduced by formate *unfused*.

(*a*). 10·47233 NH_4Br = 11·53416 Ag ∴ NH_4Br = 97·994.

Same, but the silver *fused* on pure calcium phosphate cupel.

(*b*). 4·91997 NH_4Br = 5·41834 Ag ∴ NH_4Br = 98·0028.

V. Ammonia from ammonium sulphate. Hydrobromic acid from pure bromine. *Second* crop of crystals. Silver reduced by formate.

The ammonium bromide was sublimed in a current of pure ammonia, and allowed to cool for 4 hours in it at the atmospheric pressure, then left in a vacuum for 36 hours over sulphuric acid. It was then divided into two portions, one of which was left 54 hours longer over sulphuric acid in a vacuum, when—

(*a*). 5·00442 NH_4Br = 5·51164 Ag ∴ NH_4Br = 97·997.

The other portion was dried as usual in hydrogen and ammonia at 180°, when—

(*b*). 5·17914 NH_4Br = 5·70390 Ag ∴ NH_4Br = 98·000.

VI. In order to test in the severest manner possible the quality of the silver employed, at the suggestion of Prof. Dewar I reduced the silver bromide obtained in Series IV. (*a*) by pure hydrogen; one part of this was fused on a pure calcium phosphate cupel by means of a mouth blowpipe of glass fed by pure hydrogen, and cooled in hydrogen, then thoroughly cleaned by treatment first with pure hydrochloric acid and then with ammonia, and heated for some time in hydrogen. When compared with the ammonium bromide of Series IV. it was found—

(*a*). 4·84099 NH_4Br = 5·33177 Ag ∴ NH_4Br = 97·995.

The other portion was fused on a cupel of pure lime made as Richards recommends by igniting a mixture of 3 parts of pure lime and 1 part of pure calcium nitrate, and treated as above. It was weighed and then heated for nearly an hour in a Sprengel vacuum at the boiling point of sulphur, and afterwards to as high a temperature as the combustion tube would stand, and cooled in the vacuum. Its weight was unchanged, and no gas was extracted from it.

(*b*). 5·10677 NH_4Br = 5·62515 Ag ∴ NH_4Br = 97·984.

This seems to corroborate the statement of Stas that the silver fused on calcium phosphate is purer than that fused on pure calcium oxide. It also looked more brilliant, although the dulness of that fused on the lime was due partly to a small quantity of lime dust floating on the surface.

The silver bromide precipitated was collected after several of the titrations, in order to determine whether the silver and the bromine were strictly comparable with those of Stas. To ensure the whole of the silver being precipitated, a few drops of pure hydrobromic acid were always added. The silver bromide was collected in a porcelain Gooch crucible on a filter of the finest asbestos, which had been very carefully purified by means of sulphuric and nitric acids. It was then heated to 180°, and after an hour or so at this temperature was dried perfectly, even with the largest quantities collected. Fusion of the bromide resulted in the loss of a few tenths of a milligramme only, which by blank experiments was shown to be due to the asbestos filter. No difficulty was encountered in getting both the crucible and filter, and these together with the silver bromide and chloride, to give weights constant to one-tenth of a milligramme.

The whole of the filtrate was evaporated to dryness in each case to see if any foreign matter could be detected, or if any silver bromide had passed through. In only one case was anything weighable found, and that was in the case of the silver reduced by means of cuprous ammonium sulphite (Series III.) when 0·0018 grm. of ferric oxide was obtained. The weights of silver bromide are obviously more likely to be too low than too high from experimental errors.

II. (*b*). 6·82315 Ag gave 11·87733 AgBr.
∴ 100 Ag = 174·074 AgBr.
Stas found 174·080.

III. 9·66809 Ag gave 16·82816 AgBr.
∴ 100 Ag = 174·059 AgBr.
corr. for Fe_2O_3 174·090.

IV. (*b*). 5·41906 Ag gave 9·43315 AgBr.
∴ 100 Ag = 174·0735 AgBr.

V. (*a*). 5·51258 Ag gave 9·59596 AgBr.
∴ 100 Ag = 174 074 AgBr.

(*b*). 5·70686 Ag gave 9·93346 AgBr.
∴ 100 Ag = 174·062 AgBr.

VI. (*a*). 5·33191 Ag gave 9·28093 AgBr.
∴ 100 Ag = 174·064 AgBr.

(*b*). 5·62572 Ag gave 9·79254 AgBr.
∴ 100 Ag = 174·007 AgBr.

A further interesting corroboration of the value found above for ammonium bromide as it involves different samples of ammonia, hydrobromic acid, and silver, as well as personal equation, is that in August, 1882, Mr. C. T. Heycock and the author prepared ammonium bromide which was titrated as above against silver prepared by the cuprous ammonium sulphite method, the titration being done by Mr. Heycock. The mean of two experiments, in each of which over 7 grms. were used, was 97·993.

As Mr. Heycock was working at the time on the atomic weight of rubidium, and along with Prof. Dewar I was working at the atomic weight of manganese, our object in then preparing ammonium bromide was to have a salt which we thought could be prepared easily at any time and used as a standard substance to determine the purity of any sample either of hydrobromic acid or of silver, but as our value differed from that of Stas, only these two determinations were made, and the salt condemned as unsuitable for our purpose.

Two determinations were made with ammonium chloride; the ammonia was from the purified ammonium sulphate used in the experiments on the bromide, and the hydrochloric acid was the pure acid of commerce diluted till just under constant boiling-point strength and boiled gently for some hours, a few crystals of potassium chlorate being added at intervals, all chlorine and chlorine oxides were then expelled by boiling, and the acid distilled first through a glass and then through a platinum condenser.

(*a*). 4·78257 NH_4Cl = 9·64484 Ag ∴ NH_4Cl = 53·519.
(*b*). 5·51744 NH_4Cl = 11·12810 Ag ∴ NH_4Cl = 53·513.

The silver chloride was collected from (*a*), when with the standard ammonium chloride solution added, it was found that—

4·7830 NH_4Cl gave 12·82048 AgCl.
If AgCl = 143·387 then NH_4Cl = 53·5165,

which is the mean of the two titration values. The value given by Stas is 53·532.

The situation may be thus summed up:—

The values obtained by Stas for the equivalents of ammonium bromide and chloride are 98·032 and 53·532, whereas mine are 97·995 and 53·516 respectively. That is to say, my results are in the first case 1/2650, and in the second 1/3350 lower than those of Stas, so that if I admit 1/3000 impurity in my silver this would explain the discrepancy, especially as the value for ammonium, and therefore for the atomic weight of nitrogen deduced by Stas from the bromide and from the chloride, agree so well:—

(18·075 from the chloride),
(18·077 „ bromide),

whilst my values for ammonium do not, but are 18·040 from the bromide, and 18·059 from the chloride.

But my silver and my bromine agree exactly with those of Stas as shown by the weight of silver bromide produced from a given weight of silver. Moreover, the ammonium bromide of Stas seems to have contained some foreign matter, most probably platinum, in vessels of which he largely made his preparations. I found that I could use platinum vessels *for hydrochloric* acid and chlorides, but *not for hydrobromic* acid, as the latter attacks platinum when warmed in presence of air in vessels of this material

The value for ammonium chloride calculated from the data given by Marignac (*Bibl. Univ. Geneve*, 1843, xlvi., 367), is 53·486, but I have been unable to find how he purified his silver; but it is obvious that it must have been very pure, as he found that 100 parts of silver were equivalent to 110·343 of potassium bromide, whilst Stas found (as the mean of 14 experiments) 110·345. A further proof of the purity of my silver is given in the paper on the preparation of pure hydrobromic acid above referred to, where my value for this ratio is shown to be 110·349.

I gave some of my silver to Sir W. Crookes when I had no reasons for suspecting any impurity, and he informed me that it was the purest silver he had ever tested spectroscopically, giving fewer lines than a specimen which he had until then regarded as pure, but which on comparison with mine was shown to contain traces of copper.

Every titration performed has been given above as well as every gravimetric determination with the exception of two in which some of the precipitated silver salt was unfortunately lost during transference from the bottle to the filter, these being the silver bromide in IV. (*a*) and the silver chloride in (*b*). No two determinations were made in exactly the same way throughout, even with those in the same series, but the extreme values differ very little, and in no case has any value approached that of Stas.

It is obvious that further determinations of ammonium chloride and also some of ammonium iodide must be made in order to clear up the discrepancies indicated above. Until this has been done it would be premature to discuss the value for the atomic weight of nitrogen as deduced from the equivalent weights of ammonium haloid salts.

Davy Faraday Research Laboratory
of the Royal Institution.

RELATIONS BETWEEN ATOMIC WEIGHT, ATOMIC VOLUME, AND MELTING-POINT.

By THOMAS BAYLEY, Assoc.R.C.Sc

It is known that a definite connection exists between the atomic weight of an element and its specific gravity and melting-point (Chem. News, vol. lxxx., p. 282). It can further be shown that a definite connection exists between these physical properties of an element and the atomic weights of other elements, which is equivalent to saying that a definite law connects the atomic weights and physical properties of all elements.

The accompanying table exhibits a connection between the A.V. (expressed by $\{\ \}$) and the absolute M.P. (expressed by $[\ ]$) of various pairs of elements and the "critical points" considered by the author (Chem. News, vol. lxxvii., p. 157) to indicate the commencement of the various cycles, or the points of temperature, on the hypothesis of atomic condensation from cooling protyle, at which the tide of evolution underwent periodic change. The A.W.'s in the table are printed without brackets, and the A.V.'s are all multiplied by 10. It may be observed with regard to those pairs between the M.P. of one element with the A.V. of another element, that when the M.P. is a measurement obtained by experiment, although connected with the A.W. by a definite law, the A.V. $\left(\frac{\text{S.G.}}{\text{A.W.}}\right)$ necessarily varies with the scale on which A.W. is expressed. For example, in the expression—

$$\frac{[M']}{\{M'\}} = A$$

$$\frac{[M'']}{\{M''\}} = A',$$

when the value of the upper term of the pair is changed to $\frac{[M'M]}{M'e}$ by alteration of scale, the value of the lower term is not proportionately altered, because—

$$\frac{\text{A.V.}}{\text{A.W.}} = \frac{\text{S.G.}}{\frac{\text{A.W.}}{\text{A.W.}}} = \frac{\text{S.G.}}{(\text{A.W.})^2}.$$

Such an alteration from A.W. to A.W.^{x} occurs in the passage from H = 1 to O = 16; and although the identity between

PERIODIC PROOFS.

(NOTE.—This table, as originally arranged, showed all analogous pairs in vertical columns, but the plan had to be abandoned for want of space. The first chart was in strict accordance with the Periodic System).

A.W. = 0.

{Sb}/Sb = 1·49 {Cr}/Cr = 1·47	[S]/S = 12·1 (Se)/Se = 12·1	[Rb]/Ro = 3·66 {B}/B = 3·73	{C}/C = 2·84 [I]/I = 3·06	{Zn}/Zn = 1·44 {Nb}/Nb = 1·42	{Cu}/Cu = 1·12 {Cd}/Cd = 1·16	{C}/C = 2·84 [Pb]/Pb = 2·91
*(N)/N = 5·64 [Te]/Te = 5·74				{Mg}/Mg = 5·83 (N)/N = 5·64		
{Na}/Na = 10·1 [P]/P = 10·2	{Sr}/Sr = 4·0 [In]/In = 3·96	{Cu}/Cu = 1·12 {Mo}/Mo = 1·16	{K}/K = 11·55 [Ag]/Ag = 11·46	[Sb]/Sb = 7·52 {Cl}/Cl = 7·52	{Mg}/Mg = 5·83 [Te]/Te = 5·74	
{K}/K = 11·53 [Ag]/Ag = 11·46 {N}/N = 11·3	{Ca}/Ca = 5·41 [Cd]/Cd = 5·31	{Al}/Al = 3·85 [In]/In = 3·96	Al/Al = 3·85 {Sc}/Sc = 3·91			

α = A.W. 7.

P/P−α = 23·5 {N}/N−α = 22·6	(Se)/Se−α = 13·27 [P]/P−α = 13·24	[S]/S−α = 15·5 {O}/O−α = 15·8 {Te}/Te−α = 1·69 {Cr}/Cr−α = 1·69	[K]/K−α = 10·45 {B}/B−α = 10·37 {Ba}/Ba−α = 2·81 Tl/Tl = 2·82	{Ti}/Ti−α = 3·27 I/I−α = 3·24	{Zn}/Zn−α = 1·61 {Sb}/Sb−α = 1·58	{Cu}/Cu−α = 1·26 {Cd}/Cd−α = 1·25

β = A.W. 22·05.

{Sb}/Sb−β = 1·83 {Nb}/Nb−β = 1·85	{Red P}/P−β = 16·5 {S}/S−β = 16·5 (Se)/Se−β = 16·8 [Bi]/Bi−β = 2·92 {Se}/Se−β = 2·94	{S}/S−β = 16·5 (Se)/Se−β = 16·8 [Rb]/Rb−β = 4·93 †{Cs}/Cs−β = 4·99	{Ba}/Ba−β = 3·18 {V}/V−β = 3·19	{Ti}/Ti−β = 5·18 [Sn]/Sn−β = 5·22	{Be}/Be−β = 3·79 {B}/B−β = 3·70	

γ = A.W. 37·09.

{Ag}/Ag−γ = 1·44 [Hg]/Hg−γ = 1·43	{Sn}/Sn−γ = 2·0 {Ce}/Ce−γ = 2·02	[Rb]/Rb−γ = 6·47 {V}/V−γ = 6·59	{Zn}/Zn−γ = 3·33 Tl/Tl−γ = 3·34	{Ba}/Ba−γ = 3·66 {Ge}/Ge−γ = 3·74

* Olszewski, 15·3; Dewar, 14·2 at B.P.
† Mencke's result (*Journ. Am. Chem. Soc.*, 1899).

PERIODIC PROOFS (*continued*).

δ = A.W. 82·21.

$$\left\{\frac{O}{\delta - O}\right\} = *2{\cdot}31 \qquad \left\{\frac{Ag}{Ag - \delta}\right\} = 4{\cdot}0 \qquad \left\{\frac{Cd}{Cd - \delta}\right\} = 4{\cdot}44 \qquad \left\{\frac{N}{\delta - Na}\right\} = 6{\cdot}22 \qquad \left\{\frac{Ca}{\delta - Ca}\right\} = 24{\cdot}4 \qquad \left\{\frac{K}{\delta - K}\right\} = 7{\cdot}77$$

$$\left\{\frac{Si}{\delta - Si}\right\} = 2{\cdot}32 \qquad \left\{\frac{La}{La - \delta}\right\} = 4{\cdot}0 \qquad \left\{\frac{Bi}{Bi - \delta}\right\} = 4{\cdot}30 \qquad \left\{\frac{P}{\delta - P}\right\} = 6{\cdot}19 \qquad \left\{\frac{Ga}{\delta - Ga}\right\} = 24{\cdot}6 \qquad \left\{\frac{S}{\delta - S}\right\} = 7{\cdot}71$$

$$\left\{\frac{Mg}{\delta - Mg}\right\} = 2{\cdot}40 \qquad \left\{\frac{Au}{Au - \delta}\right\} = 11{\cdot}7$$

$$\left\{\frac{N}{\delta - N}\right\} = 2{\cdot}32 \qquad \left\{\frac{Nb}{Nb - \delta}\right\} = 11{\cdot}3$$

ϵ = A.W. 127·33.

$$\left\{\frac{Ag}{\epsilon - Ag}\right\} = 5{\cdot}17 \qquad \left\{\frac{Zr}{\epsilon - Zr}\right\} = 5{\cdot}68 \qquad \left\{\frac{Zn}{\epsilon - Zn}\right\} = 1{\cdot}51 \qquad \left\{\frac{Zn}{\epsilon - Zn}\right\} = 11{\cdot}1 \qquad \left\{\frac{K}{\epsilon - K}\right\} = 5{\cdot}11 \qquad \left\{\frac{H}{\epsilon - H}\right\} \text{b.p.} = 1{\cdot}13$$

$$\left\{\frac{Ga}{\epsilon - Ga}\right\} = 5{\cdot}28 \qquad \left\{\frac{Br}{\epsilon - Br}\right\} = 5{\cdot}59 \qquad \left\{\frac{\text{Red P}}{\epsilon - P}\right\} = 1{\cdot}53 \qquad \left\{\frac{In}{\epsilon - In}\right\} = 11{\cdot}0 \qquad \left\{\frac{Ag}{\epsilon - Ag}\right\} = 5{\cdot}17 \qquad \left\{\frac{Cu}{\epsilon - Cu}\right\} = 1{\cdot}13$$

$$\left\{\frac{K}{\epsilon - K}\right\} = 5{\cdot}11 \qquad \left\{\frac{K}{\epsilon - K}\right\} = 3{\cdot}80$$

$$\left\{\frac{Li}{\epsilon - Li}\right\} = 3{\cdot}77$$

* Dewar's result.

the two terms of the pair is not, owing to several causes,* sufficiently exact to be disturbed by so small a change as this, it is clear that a larger change (such as expression in terms of a possible element of lower atomic weight than H) would upset the identities. There is here a suggestion of necessity for an *absolute* scale of A.W., since the system of analogous pairs cannot be accidental.

The gaps in the columns in the accompanying tables are doubtless due to the want of the necessary data for so many of the known elements, and for the—as yet—undiscovered elements of the atomic system. A relation between S.G. and M.P. might be presumed to exist, because S.G. is a function of the attractive force between atoms, and M.P. is an expression for the intensity of thermal vibration which overcomes this attraction. The relations here shown are only instances, among others; thus there is a series conforming to the general expression—

$$\frac{\text{M.P. of } M_{x'}}{\text{A.W. of } M_{y'} - \text{A.W. of } M_{z'}} = A$$

for several values of A.

DETECTION OF SELENIUM IN SULPHURIC ACID.

By AD. JOUVE.

ALL ordinary sulphuric acid contains selenium, or, to be more precise, oxidised compounds of selenium. They can even, nearly always, be detected in the pure acid supplied to laboratories, or for pharmaceutical purposes.

Among the methods for detecting selenium two are fairly sensitive. One of these consists in the use of codein, which gives an intensely blue colouration to the sulphuric solution of selenious acid. Let us remark in passing that this reaction, which is said to be characteristic of codein, is also produced by morphine. In each case its sensitiveness reaches 1/200th at the most.

The second method consists in using sulphurous acid gas passed through the sulphuric acid diluted with four times its volume of water; this must be done warm. Under these conditions the selenious acid is reduced by the sulphurous acid, and the selenium is precipitated in the red form. In this case the sensitiveness reaches a maximum of 1/10,000th.

Now in what state does the selenium exist in the sulphuric acid? It exists in the forms of selenious and selenic acids. Selenic acid is only acted on with great difficulty by sulphurous acid gas, and not at all by the codein reagent, from which facts errors may frequently arise.

In a research on the composition of certain gases from carbides I had occasion to pass raw acetylene over sulphuric acid, and I observed the almost constant formation of a more or less intense red colouration. This colouration can be observed when only 1/100,000th part of selenium is present.

This colouration may be due to the formation of sulphonised compounds of the carbides, or to the setting free of selenium. To make certain which, two methods can be used:—

1. Sulphuric acid containing free selenium in suspension, dissolves it when heated, taking a green colour.

2. The red liquor is diluted with water after passing C_2H_2; it is then oxidised by permanganate until the rose-colour remains constant; the excess of $KMnO_4$ is then decomposed by means of sulphite of soda in excess, and the whole then heated; through the action of the permanganate the selenium is changed to selenious acid, which is again converted into selenium by the sulphite of soda, and, as a matter of fact, on heating we obtain a slight flocculent red precipitate of selenium, which can be collected on a filter, and identified by the odour it gives on burning, or by its solubility in the alkalis; or again by suspending it in sulphuric acid, and heating, when it dissolves with a beautiful green colour.

The reduction of the compounds of selenium is not due to the sulphonised compounds, for if we cause pure acetylene to be absorbed by sulphuric acid not giving any selenium reaction, and if we then add this solution to sulphuric acid containing as much as 1/1000th part of selenium added in the form of selenious acid, we are unable to obtain the colour reaction.

The reducing action is partly due to impurities in the

* Such as irregularity in the temperatures at which the determination of S.G. are made, allotropism, and errors of experiment.

raw acetylene gas; this gas containing, amongst other impurities, sulphide, phosphide, and silicide of hydrogen, which are all reducing agents, and which also give the colour reaction. However, when used pure these gases are not of much service; further, one of them, the most easy to obtain, viz., sulphuretted hydrogen, immediately reduces sulphuric acid with a deposit of sulphur so abundant that the selenium is entirely hidden. Pure acetylene also takes a considerable part in the precipitation of selenium, and that can be proved in two ways:—

1. The acetylene after having passed through five flasks containing pumice-stone soaked in sulphuric acid, alternated with potash tubes, gives the colour reaction when passed through a final flask containing impure acid.

2. Pure acetylene prepared from acetylide of copper gives the reaction.

It should be remarked that the sensitiveness is increased from the point of view of the rapidity of the colouration if the acetylene gas contains hydrochloric fumes.

The detection of selenium in sulphuric acid is of some interest, assuming that this acid is used in the free state, either from the pharmaceutical point of view, or under other circumstances in which it might be introduced in small quantities, for selenium compounds are far from being harmless to the human organism.—*Bull. Soc. Chim.*, Series 3, vol. xxv., No. 9.

SOME PRINCIPLES AND METHODS OF ROCK ANALYSIS.*

By W. F. HILLEBRAND.

(Continued from p. 235).

XXIII. *Fluorine.*

FLUORINE can only be estimated by the method of Rose, care being taken to use sodium-potassium carbonate as a flux, and to avoid use of the blast if possible. For minerals rich in fluorine and low in silica it may be necessary to add pure silica before the fusion in order to effect complete decomposition of the fluoride just as with the alkaline-earth phosphates. To the hot aqueous extract several grms. of ammonium carbonate are added, and more on cooling. After twelve hours the solution is filtered, ammonium carbonate is expelled, and an ammoniacal solution of zinc oxide added, whereupon evaporation is carried on till the odour of ammonia is entirely gone. After filtering, add nitric acid in insufficient quantity to fully neutralise.

The use of ammonium nitrate or chloride, instead of carbonate, for throwing out the silica and alumina is not to be recommended, because of loss of fluorine on evaporation (Rose). If the rocks are very basic it may happen that the amount of silica in the alkaline solution is so small that ammonium carbonate may be dispensed with, and the ammoniacal zinc oxide solution added at once.

By whatever modification of the method the silica and alumina may have been separated, the alkali carbonate must be converted into nitrate, and not chloride if phosphorus or chromium, or both, are present. To remove the chromium and the last of the phosphorus, silver nitrate in excess is added to the solution containing still enough alkali carbonate to cause a copious precipitate of silver carbonate, which shall take up the acid set free, and thus insure a neutral solution, and consequent complete precipitation of phosphorus and chromium. After heating and filtering, the excess of silver is to be removed by sodium or potassium chloride, and sodium carbonate is to be added, in order to furnish by addition of calcium chloride in excess to the hot solution a sufficient admixture of calcium carbonate with the fluoride. At this stage there must be no ammoniacal salts in solution, otherwise calcium fluoride may be held up.

The next operation is perhaps best conducted as recommended by Penfield and Minor (*Amer. Journ. Sci.*, 1894, Third Series, vol. xlvii., p. 389). To the gently ignited precipitate of carbonate and fluoride of calcium at most 1—2 c.m.³ of acetic acid are added in the crucible, which is then placed for a time on the water-bath, and afterwards its contents are evaporated to dryness. They are then taken up with hot water, the solution is decanted through a small filter, likewise the washings. The filter is burned in the same crucible, more acetic acid is added, and the various operations are repeated until all calcium oxide and carbonate have been extracted. The above authors find that if a great excess of acetic acid is used at the start, the results are low. While their experiments related to the determination of fluorine in a mineral rich in that element—topaz—their precautions are probably not needless with the small amounts of fluorine met with in rocks.

The well-washed and gently ignited calcium fluoride finally obtained in the course of this method should be converted to sulphate as a check upon its purity, and at the same time as a qualitative test to ascertain if it really is calcium fluoride by the characteristic odour of the gas given off. Should fluorine be found, and the weight of sulphate not correspond to that of the fluoride, the former should be dissolved in hot nitric acid, and tested for phosphorus by ammonium molybdate solution. If phosphate is absent the impurity may have been silica or calcium silicate—which of these it would be difficult to decide. In the former case the fluorine might be safely deduced from that of the sulphate, but not in the latter. If the rock were rich in sulphur it might happen that calcium sulphate would be thrown down with the fluoride, but this should be removed by thorough washing. If not, and it were certainly the only impurity present, the fluorine could be calculated, after conversion of the fluoride into sulphate, by the formula:—

$$CaSO_4—CaF_2 . 2F :: \text{Diff. between impure } CaSO_4 \text{ and } CaF_2 : x.$$

It is an exceptional case when there is exact agreement between the weight of fluoride and sulphate, and with the small amounts usually met in rocks the error may be an appreciable one in percentage of fluorine, though of no great significance otherwise.

There is no qualitative test which will reveal with certainty the presence of fluorine in rocks. Heating the powder before the blowpipe with sodium metaphosphate on a piece of curved platinum foil inserted into one end of a glass tube, or in a bulb tube, is not to be relied on in all cases. While as little as one-tenth of 1 per cent of fluorine can sometimes be thus detected with ease, much larger amounts in another class of rocks may fail to show.

XXIV. *Sulphur.*

Before proceeding to the estimation of sulphur, its condition, if present, should be ascertained.

Evolution of hydrogen sulphide on boiling with hydrochloric acid is evidence of a soluble sulphide, usually pyrrhotite, but possibly lazurite. Extraction of magnetic particles reacting for sulphur shows pyrrhotite to have been in part at least the source of the hydrogen sulphide. A reaction for sulphuric acid in the filtered solution indicates a soluble sulphate, usually noselite or hauynite. If the residue, when well washed and treated with aqua regia or hydrochloric acid and bromine, gives more sulphuric acid, the probable presence of pyrite is shown. Should this solution likewise show arsenic, the sulphide may be arsenopyrite, which, however, is of very rare occurrence in igneous rocks, if, indeed, it is ever found there.

For the quantitative extraction of the sulphur of soluble sulphates, simple boiling with hydrochloric acid suffices, which should be done in an atmosphere of carbonic acid if pyrites or other oxidisable sulphides are present, and

* *Bulletin of the United States Geological Survey*, No. 176.

should be finished as quickly as possible in order to minimise the error resulting from oxidation to sulphuric acid of the sulphur of sulphides, if present, by any ferric salts that may have been dissolved.

The sulphur of sulphides may sometimes be correctly determined by extraction with aqua regia or some other powerful oxidiser, but not always; so that it is better by far to fuse with sulphur-free sodium carbonate and a little nitre over the Bunsen burner, and for a few moments over the blast, fitting the crucible into a hole in asbestos board (Lunge) to prevent access of sulphur from the flame. After thorough disintegration of the fusion in water, to which a drop or two of alcohol has been added for the purpose of reducing manganese, the solution is filtered, and the residue washed with a dilute solution of sodium carbonate. In the filtrate (100—250 c.m.³ in bulk) the sulphur is precipitated at boiling heat by barium chloride in excess after slightly acidifying by hydrochloric acid. Evaporation to dryness first with acid, in order to eliminate silica, is needless, for in the above bulk of solution there will almost never be the least separation of silica with the barium sulphate. It is well that this is so, for evaporation on the water-bath heated by gas to remove silica would in many cases involve an error fully equal to the sulphur present by contamination from the sulphur of the gas burned.

Owing to the small amount of sulphur in rocks, special purification of the barium sulphate obtained is hardly ever needful, especially as it has been precipitated in absence of iron. Should there be fear of a trace of silica being present, it can be removed by a drop of hydrofluoric and sulphuric acids before weighing the barium sulphate.

This, of course, gives the total sulphur in the rock. If soluble sulphates and sulphides as well as insoluble sulphates and sulphides are present together, the sulphur of the first is found in solution after extraction by hydrochloric acid in a carbon-dioxide atmosphere, and that of the decomposable sulphides by collecting the hydrogen sulphide evolved.* In the residue the sulphur of the insoluble sulphides can be estimated, or from the total sulphur found in another portion its amount can be calculated. The error involved in the above estimation of the sulphur of soluble sulphides, due to the possible reducing effect of hydrogen sulphide on ferric salts, is probably negligible. Most of the hydrogen sulphide would be expelled before any such action could take place, and probably before the ferric salts were largely attacked, but of course the small proportion of sulphur set free as such from pyrrhotite would escape estimation, and introduce further uncertainty. In general, it would be safe enough to assume the composition Fe_7S_8 for pyrrhotite. However carefully all these separate determinations may be carried out, the final figures for ferrous and ferric oxides can hardly be regarded as more than approximations when much sulphide is present. (See p. 220).

(To be continued).

THE VOLUMETRIC ESTIMATION OF COPPER AS THE OXALATE, WITH SEPARATION FROM CADMIUM, ARSENIC, TIN, AND ZINC.†

By CHARLES A. PETERS.

(Concluded from p. 231).

Separation from Cadmium.

BOURNEMANN (*Chem. Zeit.*, xxiii., 565) has used nitric acid for a rough separation of copper from cadmium. This method was tried for a quantitative separation in the presence of 6 to 10 per cent strong nitric acid. The results are found in Section F of Table III. Experiments 33 to 35 stood six hours before filtering. Experiments 36 and 37 stood over night. Copper is separated from more than twice its weight of cadmium, and the results are accurate.

Separation from Arsenic in both Conditions of Oxidation.

For the separation from arsenic, arsenious oxide dissolved in sodium carbonate, and di-hydrogen sodium arseniate were the forms of arsenic used. The results are accurate, and are given in Sections G and H (Table III.). In Experiments 38 to 40 and 44 and 45 no nitric acid was added. While the presence of the nitric acid is not necessary for the separation of the copper from the arsenic, still the filtration in the absence of the nitric acid is so slow as to be objectionable. The presence of the nitric acid causes the precipitate to come down in a coarser condition, and in such condition it filters easily and is capable of being washed quickly.

Separation from Tin, in both Conditions of Oxidation.

For the separation of copper from tin, a preparation of stannous chloride (20 c.m.³ giving 0·3746 grm. metallic tin by the battery), containing sufficient hydrochloric acid to prevent deposition of oxy-salts, was used. The solution of stannic chloride contained 1·0 grm. metallic tin to every 10 c.m.³, and was used without hydrochloric acid. The results of the work are found in Sections I and K of the Table. The experiments go to show that while copper may be separated from small amounts of tin as stannous chloride, yet there is a limit to the amount of tin which may be present. One-tenth of a grm. of metallic tin is the largest amount that can be present, with 0·15 grm. copper oxide taken as the sulphate, without significant error. Practically the same statement can be made of the separation of copper from tin taken as stannic chloride. Experiment 57 shows a greater loss of copper when the nitric acid is omitted.

Separation of Copper from Iron.

A solution of ferric nitrate was used for the work on the separation of copper from iron. Low results were obtained when a solution of ferrous or ferric sulphate was used as the source of iron. The results of the experiments are recorded in Section L of the table, and show that 0·20 grm. copper oxide, as the sulphate, may be separated from 0·2 to 0·3 grm. iron oxide taken as the nitrate. In Experiment 64 a good result was obtained when no nitric acid was present, save that added in combination with the iron. A comparison of Experiments 63 and 65 shows that it is best to avoid the use of large amounts of nitric acid when the larger amounts of ferric nitrate are present.

For a practical application of the above separation of copper from iron, a convenient amount of finely-ground chalcopyrite (0·5 grm.) was roasted two to three hours in a porcelain crucible until all sulphur was driven off, washed into a beaker, strong nitric acid about 5 c.m.³ was added, and, with the beaker covered, allowed to evaporate slowly on a hot plate nearly to dryness. A little dilute nitric acid was added, the solution was filtered, the residue was washed with water containing dilute nitric acid, the filtrate (about 50 c.m.³ in volume) was precipitated with 2·0 grms. oxalic acid, and the precipitate was estimated after standing twelve to sixteen hours, as previously described. The washing with water acidified with nitric acid is important, because the finely-ground ferric oxide remaining undissolved passes through the filter when washed with water alone, but gives no trouble if the water be acidic. The results of two estimations are here given.

Chalcopyrite. Grm.	Copper found by battery. Per cent.	Copper found by oxalate method. Per cent.	Difference. Per cent
0·5000	31·00	30·92	−0·08
1·0000	31·00	31·25	+0·25

Separation of Copper from Zinc.

The separation of copper from zinc was not altogether successful, owing to the tendency of the zinc oxalate to

* With pyrrhotite a small fraction of its sulphur—one-eighth if the formula Fe_7S_8 is adopted—is liberated as free sulphur, and not as hydrogen sulphide.

† Contributions from the Kent Laboratory of Yale University From the *American Journal of Science*, vol. x., No. 59.

TABLE III. (*continued*).

	CuO taken as $CuSO_4$. Grm.	Element from which copper was separated. Grm.	Oxalic acid. Grms.	HNO_3 (sp. gr. 1·40). C.m.³.	Volume at precipitation. C.m.³.	CuO found. Grm.	Error. Grm.
				F.			
		CdO taken as $CdSO_4$.					
33.	0·1990	0·10	2·0	5·0	60	0·1983	−0·0007
34.	0·1990	0·20	2·0	5·0	65	0·1987	−0·0003
35.	0·1990	0·30	2·0	5·0	70	0·1987	−0·0003
36.	0·0398	0·40	2·0	5·0	75	0·1994	+0·0004
37.	0·1990	0·50	2·0	5·0	80	0·1996	+0·0006
				G.			
		As_2O_3 taken as Na_2AsO_3.					
38.	0·1990	0·10	2·0	—	55	0·1991	+0·0001
39.	0·1990	0·20	2·0	—	60	0·1987	−0·0003
40.	0·1990	0·50	2·0	—	75	0·1986	−0·0004
41.	0·1990	0·10	2·0	5·0	60	0·1994	+0·0004
42.	0·1990	0·20	2·0	5·0	75	0·1992	+0·0002
43.	0·1990	0·60	2·0	5·0	85	0·1995	+0·0005
				H.			
		As_2O_5 taken as H_2KAsO_4.					
44.	0·1990	0·10	2·0	—	60	0·1985	−0·0005
45.	0·1990	0·20	2·0	—	70	0·1990	±0·0000
46.	0·1990	0·10	2·0	5·0	65	0·1990	±0·0000
47.	0·1990	0·20	2·0	5·0	75	0·1992	+0·0002
48.	0·1990	0·30	2·0	5·0	85	0·1985	−0·0005
49.	0·2030	0·30	3·0	5·0	85	0·2026	−0·0004
				I.			
	Cu taken as $CuSO_4$.	Sn taken as $SnCl_2+HCl$.				Cu found.	
50.	0·1590	0·0468	2·0	5·0	55	0·1581	−0·0009
51.	0·1590	0·0936	2·0	5·0	60	0·1603	+0·0013
51*a*.	0·1590	0·0936	2·0	5·0	60	0·1591	+0·0001
52.	0·1590	0·0936	2·0	5·0	60	0·1594	+0·0004
53.	0·1590	0·1873	2·0	5·0	65	0·1603	+0·0013
54.	0·1590	0·2809	2·0	5·0	70	0·1914	+0·0324
55.	0·1590	0·2809	3·0	5·0	75	0·1988	+0·0398
				K.			
		Sn taken as $SnCl_4$.					
56.	0·1590	0·10	2·0	5·0	55	0·1581	−0·0009
57.	0·1990	0·10	2·0	—	55	0·1565	−0·0025
58.	0·1590	0·20	2·0	5·0	55	0·1577	−0·0013
59.	0·1590	0·50	2·0	5·0	60	0·1562	−0·0028
				L.			
	CuO taken as $CuSO_4$.	Fe_2O_3 taken as $Fe(NO_3)_3$.				CuO found.	
60.	0·1990	0·136	2·0	5·0	60	0·1987	−0·0003
61.	0·1990	0·272	2·0	5·0	60	0·1983	−0·0007
62.	0·1990	0·364	2·0	5·0	60	0·1988	−0·0002
63.	0·1990	0·544	2·0	5·0	65	0·1971	−0·0019
64.	0·1990	0·272	2·0	—	60	0·1995	+0·0005
65.	0·1990	0·544	2·0	2·0	60	0·1998	+0·0008
66.	0·1990	0·218	2·0	2·0	65	0·1999	+0·0009
				M.			
		ZnO taken as $ZnSO_4$.					
67.	0·1990	0·028	2·0	5·0	60	0·2007	+0·0017
68.	0·1990	0·057	2·0	5·0	65	0·2008	+0·0018
69.	0·1990	0·057	2·0	5·0	65	0·2008	+0·0018
70.	0·1990	0·085	2·0	5·0	70	0·2035	+0·0045

come down with the copper oxalate. Some experiments are given in Section M of the table.

The separations of copper from bismuth and antimony were unsuccessful.

The work may be briefly summarised as follows:—Copper, exceeding in amount the equivalent of 0·0128 grm. of the oxide to 50 c.m.³ of solution as the sulphate, may be separated completely, even in the presence of a moderate amount of strong nitric, by the addition of sufficient amount of oxalic acid.

Copper may be separated from cadmium, arsenic, iron, and small amounts of tin, when precipitated by oxalic acid in a volume of 50·0 c.m.³ containing 5 c.m.³ strong nitric acid. Inasmuch as the completeness of precipitation of the copper depends upon the presence of a certain minimum amount of the copper salt, this method is not applicable when the amount of copper falls below 0·0128 grm. of the oxide to 50 c.m.³ of solution.

The author wishes to thank Professor F. A. Gooch for much kind help given in the preparation of this paper.

ON THE RESULTS OF A SEARCH FOR OTHER SUGARS THAN XYLOSE AND DEXTROSE IN THE PRODUCTS OF THE HYDROLYSIS OF WOOD FROM THE TRUNKS OF TREES.*

By F. H. STORER, Professor of Agricultural Chemistry.

SEVERAL years ago I had occasion (*Bull. Bussey Inst.*, 1897, ii., 386) to call attention to the fact that not infrequently undue prominence has been given to the opinion somewhat widely held by botanists, and by chemists also, that an abundance of starch is stored in winter as a "reserve matter" in the wood of many kinds of trees. In reality, there is much less starch in the trunk-wood of trees growing in temperate or northern climates than has ordinarily been supposed. Hence the need of studying anew the general question:—What are the reserve matters in trees? As well as the specific question:—Whence comes the sugar which is found in the spring in the sap of many kinds of trees?

It is to be remarked that the false impression as to the presence of much starch in woods depended primarily on the use of improper methods of analysis for estimating the starch (*Bull. Bussey Inst.*, 1897, ii., 391); though it is not improbable that too much importance may sometimes have been accorded to the microscopical observations of botanists on the presence of starch in the twigs of trees. In so far as the life of the whole tree is concerned, it may perhaps be true that the reserve starch stored in twigs should be regarded in some sort as a matter of merely local significance.

It is true of course that the wood of the trunks of trees often or even usually contains in store some starch, and that in the bark also there can be found small quantities of sugars and of substances, such as glucosides, which may be capable of reducing cupric oxide after they have been subjected to the action of water, diastase, and a dilute acid, as happens in the process of analysis which depends on the application of malt. But inasmuch as the visible effect produced by matters held in store in trees is often out of all proportion greater than can be credited to the small quantities of starch and glucosides exhibited by analysis, it seems probable that there must be other carbohydrates stored habitually in trees as reserve matters, and that some of them are equally important with starch, or possibly more important, as a means of carrying forward the life of the tree from one year to another.

It has been suggested not infrequently that the cellulose or, better still, some of the hemicellulose in plants should be regarded as capable of supplying matters for the sustenance of the plant, and this idea is supported by the fact that cellulose yields dextrose when subjected to the action of strong acids, and that several observers have noticed that it is often acted upon by enzymes of one kind or another. (J. R. Green, "The Soluble Ferments and Fermentation," Cambridge, 1899, pp. 84—103).

It would be a matter of no little interest to determine what other substances (if any) beside cellulose that are capable of yielding sugars by hydrolysis could be detected in woods, and the motive of the research here described was to ascertain if possible whether any suggestions as to the presence in woods of substances hitherto undetected could be got by testing roughly though methodically the reducing power and the rotatory power of various products obtained by hydrolysing woods with acids.

It was found by preliminary trials that after xylan had been removed (in some part) by boiling the powdered woods in dilute acids, it is easy to obtain no inconsiderable quantities of sugar by treating the residual wood with strong acids, and subsequently diluting and boiling the mixture. On neutralising and decolorising (if need were) these solutions, after the hydrolysis, they were tested quantitatively for sugar, by means of Fehling's liquor, and their rotatory power was observed with a Schmidt and Haensch polariscope.

Inasmuch as the solutions necessarily contained, beside sugar, extractive matters of one kind or another, it would have been impracticable to determine the specific rotation in each case by the usual and conventional method; for, in order to do that, we need to know the quantity of sugar that is contained in a determined weight of the solution, while in the method here employed we can find only the quantity of sugar in a measured *volume* of the solution. But it is still possible to compare these determinations one with another, and to obtain an approximation to the true specific rotation by making use of the formula—

$$[\alpha]_D = \frac{a \times s}{l \times g}, \text{ in which}$$

a = the observed angle;
l = the length of tube;
g = the number of grm. of dextrose in s, as determined by Fehling's liquor;
s = the number of c.c. of the saccharine solution taken.

I have designated these approximate rotations as "quasi-$[\alpha]_D$," and it is to be observed that the results set forth in this article have all been obtained in this way, unless otherwise expressly stated.

It should be observed that although the figures of the quasi-rotations are always somewhat higher than those of the true specific rotations, they must nevertheless depend upon definite relations which subsist between the quantities of sugar detected in the solutions and the angles of rotation actually observed in the polariscope.

For the sake of illustration a sample of pure dextrose was tested in the manner and by the formula above stated, and there was obtained as the approximate specific rotation of this substance, quasi-$[\alpha]_D = 56{\cdot}84°$; while pure galactose (from Merck and Co) treated in the same way, gave quasi-$[\alpha]_D = 86°$.

Whereas, the true specific rotations $[\alpha]_D = 53{\cdot}40°$ (for dextrose), and $[\alpha]_D = 79{\cdot}94°$ (galactose), were obtained on testing these very samples in the conventional way, and calculating from the observed data by means of the proper formula, viz.:—

$$[\alpha]_D = \frac{a(p+q) \times 1{\cdot}00125}{p \times d \times l}, \text{ in which}$$

a = the observed angle;
p = the number of grm. of sugar;
q = the number of grm. of water;
l = length of the tube;
d = sp. gr. of the solution at 17·5°;
1·00125 = factor for reducing the sp. gr. to 4° C.

In the preliminary trials above mentioned, it appeared as a rule that the rotatory power exhibited by the products of hydrolysis was appreciably higher than could have been the case if only dextrose had been present. Thus, several specimens of maple wood, hydrolysed as above described, after the action of strong acid, and tested in the manner indicated, gave the results which here follow:—Quasi-$[\alpha]_D = 63°$, 65°, 66°, 68°, 69°, and 73·5°, respectively. Birch wood, similarly treated, gave quasi-$[\alpha]_D = 64{\cdot}5°$; and pine wood gave quasi-$[\alpha]_D = 71°$.

It was with the hope of explaining this matter that systematic experiments upon maple and birch woods, and upon cotton cloth also, were made, as is described on the following pages:—

A. *An Examination of the Products of the Acid Hydrolysis of Wood from the Trunk of a Sugar Maple Tree (Acer saccharinum).*—10 grms. of maple wood in fine powder taken from the outer part (wholly free from bark) of the trunk of a tree four inches in diameter, felled on May 30th in the West Newfield, Maine, were soaked during twenty-four hours in 200 c.c. of strong ammonia water, to remove colouring matter and albumenoids, and were then thrown upon a filter, and washed with water. Enough dilute hydrochloric acid, of 3 per cent, was poured

* *Bulletin of the Bussey Institution*, 1900, vol. ii., Part 9.

into the filter to displace the moisture retained by the wood, and the latter was then boiled in a flask, with reflux condenser, over a free flame, with 200 c.c. of hydrochloric acid of 3 per cent during 3·5 hours. The undissolved wood was removed by filtration, and one half the product of the hydrolysis was neutralised with sodium hydroxide, and decolorised with bone-black. On testing the solution with Fehling's liquor it appeared that 100 c.c. of it reduced as much cupric oxide as would have been reduced if the solution had contained 0·5669 grm. of dextrose. This quantity would be equal to 16·21 per cent of dextrose in the dry wood. On observing in the polariscope through a 2 dm. tube a rotation of 0·5° was noted, *i.e.*, quasi-$[\alpha]_D = 44·09$.

The other half of the liquid that had been removed from the wood was boiled 3·5 hours longer over a free flame, and was then neutralised and decolorised as before. The specific rotation in this case was quasi-$[\alpha]_D = 68·17°$, and Fehling's liquor showed "sugar" (calculated as dextrose) equal to 10·43 per cent of the dry wood.

Due allowance being made for the possibility of the presence in the solution of matters other than sugars, which might have some influence on the rotatory power, it is to be presumed that the sugar observed in the product of the first hydrolysis probably consisted of a mixture of xylose and dextrose, and that some of the latter was made to "revert" to compounds of higher rotatory and lower reducing powers by the second boiling, after the removal of the wood. Such reversion has repeatedly been noticed by chemists,* and there are researches by Grimaux and Lefèvre (*Comptes Rendus*, 1886, ciii., 146), by Gautier (*Bull. de la Soc. Chim. de Paris*, 1874, xxii., 145), and by Fischer (*Ber. der Deut. Chem. Gesell.*, xxiii., 3687; xxvi., 2400; xxvii., 2478; xxviii., 1145, 1167, 3024), which help to explain what kinds of products are formed.

The residual wood, taken from the acid liquor of these first trials with dilute acid, was soaked in strong hydrochloric acid of 35 per cent, during twenty-four hours, and the mixture was then poured into boiling water, taken in such quantity that the final strength of the acid in the mixture should be 3 per cent. In the 3 per cent acid thus obtained, the residual wood was boiled over a free flame during six hours. The liquid was then neutralised with sodium hydroxide, evaporated, and decolorised with bone-black. The specific rotation was found to be quasi-$[\alpha]_D = 70·84°$, and Fehling's liquor showed 3·79 per cent of "dextrose" calculated on the material operated upon or to 3·17 per cent of the dry wood.

The wood left after the foregoing treatments with hydrochloric acid was rubbed up with 10 c.c. of concentrated sulphuric acid (of 92·5 per cent H_2SO_4), and the dark brown mixture was left to itself during twenty-four hours: it was then poured into enough boiling water to yield an acid containing 3 per cent of H_2SO_4, and was boiled therein during 3·5 hours. After filtration a part of the liquid was neutralised with sodium hydroxide. It was clear enough to be examined without the use of decolorising agents. It gave quasi-$[\alpha]_D = 66·16°$ and "dextrose" amounting to 33·50 per cent of the dry residue or to 27·04 per cent of the dry wood. This solution may be called "A." Another portion of the filtered acid liquid was boiled 3·5 hours longer, without any further addition of acid, and was then neutralised with calcium carbonate, filtered, and evaporated. The solution was clear enough to be examined without decolorising it. The approximate specific rotation was quasi-$[\alpha]_D = 64·82°$, and the "sugar," as shown by Fehling's liquor, and calculated as dextrose, amounted to 35·08 per cent of the dry residue. This solution may be called "B."

The high rotatory power exhibited by these products of the hydrolysis of wood, taken in connection with other results of similar import which had been obtained previously while studying other specimens of woods, pointed most distinctly to the presence of some other reducing substance beside dextrose and xylose; for the true specific rotation of xylose is $[\alpha]_D = 19·2°$, and that of dextrose is $[\alpha]_D = 52·6°$ (Tollens, "Handbuch der Kohlenhydrate," 1895, ii., 5). Efforts were made at once to isolate this additional substance. To this end a part of each of the sulphuric acid solutions "A" and "B" were allowed, after neutralisation, to evaporate spontaneously (in mid-winter) at the ordinary temperature of the laboratory. From "A" crystals of sodium sulphate separated, and were removed. The brown residues from the evaporation were rubbed up with three successive portions of strong alcohol. A part of the matter dissolved, while there was left a sticky, stringy, dextrin-like mass, insoluble in strong alcohol, though readily soluble in cold water. The aqueous solution of this substance had a flattish, sweetish taste, as was noticed in other instances. That from "A" gave quasi-$[\alpha]_D = 89·69°$. Meanwhile, the matter soluble in alcohol, obtained from "A," was taken up with water after the alcohol had been driven off, and this solution gave quasi-$[\alpha]_D = 66·18°$, calculated as dextrose, as was the preceding.

From the solution "B," which was boiled in the dilute acid longer than "A" had been boiled, a somewhat different result was obtained. The matter left undissolved by strong alcohol in this case was not wholly soluble in water. The insoluble residue was granular rather than gummy, and the solution obtained by means of water had practically no reducing action on Fehling's liquor.

The matter soluble in alcohol in this case gave quasi-$[\alpha]_D = 69·57°$, when examined in aqueous solution, and calculated as dextrose. It is evident from the foregoing that that product of the hydrolysis which fails to dissolve in strong alcohol (as in "A") is apt to suffer decomposition when boiled for a long time in dilute acids. It will be noticed that in all these experiments no wood was left in contact with the acid during the second boilings; the acid then had nothing to act upon but the products formed by the first boiling. The nature of this decomposable substance will be discussed in subsequent paragraphs.

(To be continued).

* Compare for example, the memoir of Wohl in *Ber. der Deut Chem. Gesell.*, 1890, xxiii., 2095, and Wohl's list (on p. 2084) of the names of chemists who have worked upon the subject.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING APRIL 30TH, 1901.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, May 10th, 1901.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 192 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from April 1st to April 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 192 samples examined by us during the month, all were found to be clear, bright, and well filtered.

For the first time in the present year, the monthly rainfall at Oxford shows an excess, the amount of rain measured during April was 1·96 inches; the average fall is 1·61 inches, giving an excess of 0·35 inch, and reducing the deficit for the year to 1·21 inches, or 17·3 per cent on the thirty-five years' average.

Our bacteriological examinations of 483 samples have given the results recorded in the following table; we have also examined 36 other samples, from special stand-pipes, &c., making a total of 519 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 24 samples) ..	176
New River, filtered (mean of 122 samples) ..	6
Thames, unfiltered (mean of 23 samples) ..	2076
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 257 samples)	15
Ditto ditto .. .. highest	196
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 24 samples) ..	177
River Lea, from the East London Company's clear-water wells (mean of 33 samples) ..	15

Of the 412 samples of impounded and filtered water supplied to London, examined bacteriologically during the past month, twenty-six samples, or 6·3 per cent, were sterile. Only one sample out of the total number examined contained more than 150 microbes, and only six, or 1·4 per cent, contained more than 100 microbes per c.c. The mean of the microbes in the excess samples was 126, against a corresponding mean last month of 162. These bacterial results can only be characterised as excellent.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

NOTICES OF BOOKS.

Atoms and Energies. By D. A. Murray. New York: A. S. Barnes and Co. 1901.

This remarkable book is written by a some time instructor in the Government Shogyo Gakko, Kyoto, Japan, who is now pastor of a Presbyterian church in the State of Iowa; it is endorsed in an introduction by an anthropologist, well known through his archæological investigations in Mexico.

Physicists and chemists seekling novel ideas will find in this essay food for thought and reflection; they are told that chemical affinity is the result of the *shapes* of atoms, that atoms are in actual contact, that the number of points of contact determines the state of aggregation; thus, "when the atoms are not in contact we have the gaseous state, when but a single point of contact the liquid state, when so many points of contact there is rigidity the solid state, when face to face contact chemical combination." All atoms are identical in essence; they are influenced by two simple energies, gravitation or attraction, and heat or expansion; "both are distinct entities articulated to, but not a quality or attribute of, atoms."

The author's definition of an atom is interesting:—"An impenetrable expanse of the ability to modify and be moved by energy." B.

Annual Report of the Smithsonian Institution for 1899.

One of the functions of the Smithsonian Institution, at Washington, is the diffusion of knowledge in language "understanded of the people;" so that, while most of its works are intended primarily for the specialist, the Secretary publishes an Appendix to his Annual Report which is addressed to the large body of the public, which has a general interest in scientific matters though without special knowledge of them.

The Report for 1899, just issued by the Institution, contains thirty articles, covering a wide range of information, given in such terms as must interest the general reader. They mainly refer to the scientific novelties of the year, and are selected because they are interesting as well as sound expositions of the most important scientific results that the year has brought. We have, for instance, an account by Professor Dewar, of the Royal Institution of Great Britain, of the recent liquefaction of hydrogen and of work on temperatures as low as 250 degrees centigrade below zero. There is a most curious and interesting paper by Johnstone Stoney on the range of Nature's operations. The volume contains two papers by Sir William Crookes, at once President of the British Association for the Advancement of Science, and of the Society for Psychical Research. In the one he presents the startling idea that there may be means of communication between human minds without the intervention of any of the ordinary channels of sense. In the other there is an interesting discussion of the effects which a simple change of scale would make on our understanding of Nature. He imagines our full human intelligence to exist in a body so small in size that to it the world of Lilliput would be a world of giants, and indicates conclusions which are altogether surprising and unexpected. The paper first mentioned is a departure from the usual rule of the Smithsonian publications, and is prefaced by a special note by Secretary Langley to the effect that while these commonly set forth known and admitted scientific facts, and not speculations, these articles are so weighty that an exception is made in their favour, though it is added that they are not presented as demonstrated. Their reprinting here may be taken as a curious sign of the times, illustrating the fact that men of science now hold an open mind toward speculations which a generation ago would have been scoffed at in the same circles.

A very comprehensive review of nineteenth century science, by Sir Michael Foster, the friend of Huxley and editor of his works; a most interesting paper on the extinct mammoth, by Mr. Lucas; a review of the subject of the date of the Calaveras skull, by Mr. Holmes, who leans to the opinion that it is of a modern Californian and not of a prehistoric man; two well illustrated papers on the peopling of the Philippines, by Virchow, and a list of native tribes of the Philippines, and of the languages spoken by them, by Blumentritt, the greatest living authority on the ethnology of the Philippines; an account by Professor Lester F. Ward of the petrified forest of Arizona, and other papers not only instructive, but entertaining, which cannot be more especially mentioned, are contained in this volume, which is profusely illustrated with plates and maps.

The Smithsonian Reports are distributed by the Institution to libraries throughout the world, may be had by purchase at cost from the Superintendent of Documents, Washington City, and may generally be obtained free of charge, also from the applicant's Member of Congress.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxii., No. 17, April 29, 1901.

Variation in the Composition of Mineral Waters.—P. Th. Muller.—For a complete study of a water, a chemical analysis is indispensable, and nothing can take its place. The composition of a natural water is not necessarily invariable. It varies with the season of the year, and from year to year, and also permanently alters during several years. The author's experiments were carried out on the dissolved matter in certain waters. He

measured in all cases the electrical conductivity by the method of alternating currents and the telephone, operating always at the same temperature (about 25°). The conductivity depends on the nature and the quantity of the dissolved substances, and its measurement should precede a chemical analysis of a mineral water. The author's researches, which extended over a year, were taken upon the conductivity of the water from one of the sources of the Vosges.

Myrcenol and its Constitution.—Ph. Barbier.—By the hydratation of myrcene an alcohol of formula $C_{10}H_{18}O$ is obtained, to which the name myrcenol has been given. This substance is an oily liquid, colourless, and having a powerful smell; its boiling-point is 99—100° at 10 m.m. pressure, and its density at 14·5° is 0·9012. The author's experiments on this substance satisfactorily establish its constitution, which may be represented by the formula $CH_3-C=CH-CH_2-CH_2-C(OH)-CH=CH_2$ (with CH_3 and CH_3). This formula shows that the substance is of the tertiary alcoholic nature. A knowledge of the constitution of myrcenol easily leads to that of myrcene, which can be obtained by dehydratation of the former, and so has the constitution $CH_3-C=CH-CH_2-CH=C-CH=CH_2$ (with CH_3 and CH_3).

Ethyl Nitroacetate.—A. Wahl.—The potassium and sodium salts of ethyl nitromalonate, $C_7H_{10}NO_6K$ and $C_7H_{10}NO_6Na$, can be obtained in the form of large yellow needles, soluble in water. When heated on platinum, these crystals first melt and then explode with extreme violence. Either of these salts, when treated with dilute acids, gives ethyl nitromalonate, which can be purified by distillation under reduced pressure. The substance thus prepared is a colourless liquid, analysis showing it to have the formula $C_4H_{10}N_2C_4$.

Preparation of Isomeric Ortho-, Meta-, and Para-nitrobenzoylcyanacetic Ethers and Crystallised Ortho-nitro-benzoyl Chloride.—M. Mavrojannis.—When nitrated benzoyl chlorides react on sodium cyan-acetic ether, the author succeeded in preparing the ortho-, meta-, and para-nitrobenzoylcyanacetic ethers. These bodies are formed during a reaction represented by the equation—

$$C_6H_4(COCl)(NO_2) + NaCH(CN)(COOC_2H_5) = C_6H_4(CO-CH(CN)(COOC_2H_5))(NO_2) + NaCl.$$

New Reaction of Saccharine (Benzoic Sulphimide).—Alex. Leys.—The presence of saccharine in a solution can be detected when the product of the ether extraction, taken up once again by means of water, gives a sweet taste and is limpid and not coloured after the addition of iron perchloride, but which gives a violet colouration on the addition of very dilute peroxide of hydrogen.

Contribution to Micro-chemical Researches on Alkaloids.—E. Pozzi-Escot.—The author obtains several interesting reactions, but these do not allow of a rigorous toxicological research. With strychnine, chloroplatinic acid gives prismatic plates of a peach colour. Auric chloride gives an abundant crystallisation of prisms grouped in colonies. Potassium iodide and iodine give abundant crops of crystals of a dark olive-green colour and great sharpness. With brucine, platinic chloride gives very small star-like crystals; with quinine, platinic chloride gives little grains which strongly polarise light. Iodine, dissolved in potassium iodide, gives little prisms. Platinic chloride gives, with cocaine, large toothed crystals; gold chloride gives similar crystals. With codeine, mercuric iodide dissolved in potassium iodide gives clusters of almost black crystals. Iodine in iodide of potassium with atropine gives pointed crystals, grouped in two's and crossed, of a black colour. Morphine, with the same reagent, gives crystallisations in the form of a thistle head.

MISCELLANEOUS.

Appointment.—Mr. William French, M.A. (Cantab), F.I.C., F.C.S., for the past nine years Senior Science Master of the Bury Grammar School, and of the Bury and Ramsbottom Technical Schools, was on Tuesday elected Principal of the Stevey Institute and Municipal Technical School, Lancaster. There were 135 applicants. Mr. French, who has been a frequent contributor to the Chemical News, was for twelve years Assistsnt to Prof. Liveing, F.R.S., and Prof. Dewar, F.R.S., at Cambridge, being for some time assistant to the former in private research.

The Double Nitrates of Tetratomic Cerium and of Thorium.—R. J. Meyer and R. Jacoby.—While comparing them with the double nitrates of gold examined by M. Schottländer which were regarded as the salts of a nitro-auric acid $(NO_3)_4AuH$, the authors have examined ceric nitrate and its double salts. Ceric nitrate, which was obtained by Berzelius as a syrupy yellow mass, can be prepared in the form of beautiful orange crystals, if to the solution of CeO_2 in concentrated NO_3H we add nitrate of calcium, and then leave the whole to stand in a desiccator. However, the salt obtained in this manner is a basic salt, $(NO_3)_3CeOH+3H_2O$. The ammonio-ceric nitrate, which occurs in beautiful deep red crystals, has been examined by various authors, but it has not been decided by them whether or no the salt is anhydrous; as a matter of fact it is, the formula being $(NO_3)_6Ce(NH_4)_2$. We also get salts of cæsium, rubidium, and potassium; this latter is the most difficult to obtain. All four are of the type $(NO_3)_6CeR_2$. The double salts of the magnesian series (magnesium, zinc, nickel, cobalt, manganese), belong to the same type with about the same water of crystallisation, viz., $(NO_3)_6CeM+8H_2O$; they are only slightly stable, the nickel salt appears in dark yellowish-brown crystals. The authors next directed their attention to the double nitrates of thorium, which have not yet been described; they take their rise in a mixture of two nitrates in concentrated solution; water decomposes them into their constituent parts. One of the double ammoniacal salts is $(NO_3)_5Th(NH_4)+5H_2O$; under other conditions of concentration we obtain another salt, $(NO_3)_6Th(NH_4)_2$, corresponding to the cerium salt; similar results are obtained with the anhydrous salts of cæsium and rubidium, $(NO_3)_6ThR_2$. With magnesium, zinc, nickel, cobalt, manganese, and strontium we also obtain salts corresponding with the ceric compounds, $(NO_3)_6ThM+8H_2O$. With potassium a very acid salt was obtained having a great tendency to crystallise. Beautiful crystals are formed with brilliant facets, rapidly becoming dull on exposure to the air, with loss of water and nitric acid; their composition is $(NO_3)_{10}ThK_3H_3+5H_2O$.—*Berichte*, vol. xxxiii., p. 2135.

MEETINGS FOR THE WEEK.

Tuesday, 28th.—Royal Institution, 3. (The Tyndall Lectures). "The Philosophical Undertones of Modern Poetry," by Prof. William Knight, LL.D.

Thursday, 30th.—Royal Institution, 3. "The Chemistry of Carbon," by Prof. Dewar, F.R.S., &c

Friday, 31st.—Royal Institution, 9. "With the Allies in China," by A. Henry Savage Landor.

—— Physical, 5. "On a Model which Imitates the Behaviour of Dielectrics," by Prof. Fleming, F.R.S., and A. W. Ashton, B.Sc. "On the Resistance of Dielectrics and the Effect of an Alternating Electromotive Force on the Insulating Properties of Indiarubber" and "Note on the Electrification of Dielectrics by Mechanical Means," by Mr. Ashton.

Saturday, June 1st.—Royal Institution, 3. "The Biological Characters of Epiphytic Plants." by Prof. J. B. Farmer, M.A., F.R.S.

THE CHEMICAL NEWS.

Vol. LXXXIII., No. 2166.

ANALYSIS OF THE RED RAIN DEPOSIT WHICH FELL IN VICTORIA, AUSTRALIA, ON DECEMBER 26, 1896, AND WHICH IS SIMILAR IN APPEARANCE TO THAT WHICH FELL IN ITALY IN MARCH, 1813, AND AGAIN IN MARCH OF THE PRESENT YEAR.

(Second Note).

By Dr. T. L. PHIPSON.

The very minute quantity of this deposit which was forwarded to me by Captain C. J. Gray, F.R.G.S., who collected it with great care near Melbourne, and of which I gave some account in April last (Chemical News, vol. lxxxiii., p. 159), did not permit of an exhaustive chemical examination. That gentleman, however, has kindly given me a little more, which has enabled me to throw some light on its true nature, though the analysis in this case was made on less than half a grm.

I need not repeat here what I have said in my first note of its physical properties and microscopic appearance, but will merely add that it is very slightly, if at all, magnetic.

It should be stated that the analysis given in a note in the *Comptes Rendus* (April, 1901), by M. Stanislas Meunier, of a specimen collected this year at Palermo, appears to show that some white-wash of the window-sills was scraped up with the red deposit, and that the author of that note has taken for quartz or sand what is really glassy felspar.

The deposit which was collected from the rain in Italy in March, 1813, was analysed by Sementini, then Professor of Chemistry at Naples. This analysis is also rather unsatisfactory, but it shows nothing to indicate that the red rain deposit was "sand from the Sahara Desert," as suggested in the *Comptes Rendus*. He believed it was not of volcanic, but perhaps of meteoric, origin.

This fall of red rain in 1813 was accompanied by noise compared to the dashing of waves at a distance, and some meteoric stones fell at the same time at Cutro, in Calabria.

On November 15th, 1755, *rain of a red colour* fell around Lake Constance and at Ulm, also, on the same day, in Russia and Sweden. The deposit on this occasion was stated to be *magnetic*. No analysis was made of it, as far as I know.

The general aspect and physical properties of these curious falls of mineral matter along with rain correspond very closely with each other; they are all described as a very fine dust, very soft or unctuous to the touch, of a reddish yellow or fawn colour when dry, becoming rather redder when wet and darker on being heated. I found the dimensions of the grains of which it is composed exceedingly small, a great many being flat or tabular, with irregular edges, and of various colours (see my first Note).

My analysis of the red rain deposit which fell in Australia has given the results here shown. The substance does not effervesce when HCl is poured upon it, neither does it give off chlorine.

The portion insoluble in HCl has, in 100 parts, the composition of felspar (and also the blowpipe characters) —a substance which forms part of volcanic rocks and of meteoric stones. The portion soluble in acid may be labradorite or peridot, or a mixture of both, to which the same remark applies.

It was impossible with the very small quantity of substance at my disposal to make the analysis more complete.

Water	9·09	14·30
Organic matter	5·21	
Soluble in HCl—		
Oxide of iron, alumina, silica, and titanic acid	4·61	8·00
Lime, magnesia, and alkalis, with traces of Ni and Co	3 39	
Insoluble in HCl—		
Silica	50·99	77·70
Alumina and oxide of iron (without any titanium)	16·40	
Lime..	0·21	
Magnesia..	Minute quantity	
Potash and soda, with indication of lithia	10·10	
	100·00	

I am decidedly of opinion, after a due discussion of this subject, that this dust brought down in the rain is of volcanic origin. The composition, *as a whole*, corresponds closely with that of the Puzzolana of Naples and Rome. Such volcanic dust, shot up to immense heights, may remain for years suspended in the atmosphere, and is liable at any time to be attracted by storm clouds and precipitated with the rain they yield.

Casa Mia, Putney, S.W.,
May 27, 1901.

THE ESTIMATION OF CYANIDES IN LAMING'S MIXTURE.

By A. O. NAUSS.

In view of the increasing importance of compounds of cyanogen in different branches of industry, gas works which now supply the raw material for these products are constrained to utilise this by-product as completely as possible, and, thanks to exact analytical methods, we are now able to determine its proportion in Laming's mixture with rapidity.

Among the methods of estimating cyanides there are three which may be recommended; those of Knublauch (*Journ. fur Gasbeleuchtung*, 1889, p. 450); Zulkowski (*Chem. Tech. Unters-Meth. von Lunge*, i., 492), modified; and Drehschmidt (*Journ. fur Gasbeleuchtung*, 1892, pp. 221 and 268).

Although the two former methods are very widely used and have the advantage of simplicity, they both have the inconvenience of being touch methods, in which the exact end of the reaction can only be judged with difficulty, or through long practice.

Drehschmidt's method, especially as modified by Buschell (*Journ. fur Gasbeleuchtung*, 1893, p. 8), may be looked upon as very exact, as is also the method due to Lubberger (*Journ. fur Gasbeleuchtung*, 1878, p. 124). It requires, however, a considerable amount of time, on account of the numerous operations entailed, and further, it is necessary to scrupulously remove all trace of chlorine from the reagents.

In a works laboratory the principal characteristics of an analytical method should be simplicity and exactness.

Keeping this in view, I have devised a new method of which the starting point is the decomposition of the Prussian blue by alkalis, according to the equation :—

$$Fe_7Cy_{18} + 12NaOH = 4Fe(OH)_3 + 3FeCy_6Na_4.$$

The Prussian blue is treated with a warm solution of soda of known strength until it is decolorised. Before the colour has entirely disappeared the liquid takes a

green tint. It is as well to use an excess of alkali which can be neutralised afterwards with a titrated acid solution. On the addition of an excess of acid the yellow tint of the liquid changes to greenish by reason of the re-formation of the Prussian blue.

It is not necessary to use any special indicator, as the compounds in solution take its place. It is only necessary to operate with boiling solutions; in this case the end of the reaction is very distinct and sharp. When we make use of N/50 soda the factor for obtaining the Prussian blue is 0·001431.

The method of carrying out the analysis is as follows:—

Into a flask, marked at half a litre, we place 10 grms. of Laming's mixture, and 50 c.c. of 10 per cent soda; this is frequently shaken, and the reaction allowed to proceed at the ordinary temperature. According to Knublauch (*Journ. fur Gasbeleuchtung*, 1889, p. 453), this operation requires fifteen hours. By using dilute soda we prevent the formation of alkaline sulphides. The flask is then filled up to the mark, and a further 5 c.c. of water are added, corresponding to the volume of the mixture employed, and, after having thoroughly shaken, we filter about 50 c.c.

This liquid is run into 10 or 15 c.c. of a warm acid solution of iron-alum (200 grms. of alum and 100 grms. H_2SO_4 per litre), so as to transform the ferrocyanide into Prussian blue; it is then heated on the water-bath until the characteristic sweetish odour which is produced ceases to be apparent. We then filter hot through a folded paper, and wash the precipitate with hot water until the washings no longer contain any sulphuric acid.

The filter and the precipitate are then placed in a flask, water is added, and the whole brought to boiling point with constant shaking.

We next gradually add N/50 soda until all the Prussian blue is decomposed, which does not require a very long time. The excess of soda is then titrated with N/50 acid, keeping the solution warm and agitating. It is indispensable to heat the solution, for even in the presence of an alkali, the Prussian blue will be re-formed, giving a green tint, which lasts some considerable time. When the green tint remains permanent the operation is finished.

Comparative analyses with the Drehschmidt-Burschell method and mine have given the following results:—

No.	Proportion of Prussian blue.	
	Drehschmidt.	New method.
	Per cent.	Per cent.
1.	8·11	8·08 and 8·15
2.	7·3	7·02
3.	8·86	8·65
4.	8·11	8·29
5.	7·65	7·63
6.	7·51	7·34
7.	7·63	7·72 and 7·65

I have, further, made comparative analyses after adding a known weight of ferrocyanide of potassium to Laming's mixture; there again the results were the same.

This method can be extended to the determination of cyanogen in gas.

The following method of working has given very good results:—

One hundred litres of gas are passed through two wash bottles, each containing 10 c.c. of a solution of sulphate of iron at 10 per cent, and 10 c.c. of caustic potash at 33 per cent. The length of time for this operation should be from one to two hours. The contents of the wash-bottles are then poured into a half litre flask, and potash and sulphate of iron are further added until there is no more precipitate of sulphide of iron formed. It is as well to add 1 grm. of carbonate of lead to remove all the sulphuretted hydrogen.

After boiling for a few minutes the liquid is cooled, and the flask filled up to the half litre mark; 5 c.c. more water are added to make up for the volume of the precipitate, and the whole is then filtered on a dry filter.

Fifty c.c. of the filtrate are taken, so as not to have too voluminous a precipitate; this is poured into an excess of a warm solution of iron-alum (20 or 30 c.c.); then after having heated for some time on the water-bath, sulphuric acid is added to precipitate the Prussian blue. The rest of the analysis is the same as in the case of Laming's mixture.

One c.c. of N/50 alkali corresponds to 0·0007794 grm. of cyanogen.—*Journ. f. Gasbeleuchtung und Wasser versorgung*, xliii.

SOME PRINCIPLES AND METHODS OF ROCK ANALYSIS.*

By W. F. HILLEBRAND.

(Concluded from p. 247).

XXV. *Boron.*

To the best of the writer's belief, it has never been found necessary in this laboratory to estimate boron in a silicate rock. Should the determination be required, since most silico-borates are insoluble minerals, it would probably be necessary to fuse with sodium carbonate, extract with water, faintly acidify with nitric or acetic acid, expel the boron by distillation with methyl alcohol, and collect the boric ether in a suitable manner. For simple borates, artificial or native, this method,† first devised by Rosenbladt and Gooch independently, gives entire satisfaction when all needful precautions are carefully observed, but its application to boro-silicates yet needs investigation, in view of the as yet unexplained very discordant results obtained some years ago by J. E. Whitfield in this laboratory on the mineral warwickite, a boro titanate of magnesium and iron.

It is also quite possible that the accurate estimation of but a few milligrms. or even less of boric oxide by the use of a large excess of lime as a retainer would not be feasible. Fluorine would have to be first removed by calcium nitrate or acetate before freeing the boron.

XXVI. *Nitrogen.*

Nitrogen has been found in igneous rocks or the minerals occurring in them by several observers. Thus, H. Rose ("Quantitative Analyse," p. 673, Finkener Edition), says that pitchstone gives off ammoniacal water on heating; Silvestri (*Gazz. Chim. Ital.*, 1875, vol. v., p. 303), mentions a nitride of iron in lavas from Etna; Sandberger finds ammonium carbonate to be given off from certain rocks of Pribram; the writer has shown nitrogen to exist in uraninite; Ramsay and others have noted it in traces with or without helium, &c., in numerous minerals; and later Erdmann (*Ber. Deut. Chem. Gesell.*, 1896, vol. xxix., p. 1710), found it to be given off as ammonia on treating various minerals of "ancient igneous rocks" with a caustic alkali. Luedeking also found ammonium sulphate in a barite from Missouri, the presence of which the writer was able to confirm.

It has been noted in this laboratory on three separate occasions, when series of ores, roofing slates, and eruptive rocks were analysed, that ammonia, either in the form of

* *Bulletin of the United States Geological Survey*, No. 176.

† Rosenbladt (*Zeit. fur Anal. Chem.*, 1887, vol. xxvi., p. 21), used magnesia for binding the boron, while Gooch (*Proc. Amer. Acad. Arts and Sci.*, 1886, p. 167; *Bull. U.S. Geol. Survey*, No. 42. p. 64; CHEMICAL NEWS, 1887, vol. lv., p. 7), preferred lime, as more active and reliable. Gooch and Jones have later (*Amer. Journ. Sci.*, 1899, Fourth Series, vol. vii., p. 34; CHEMICAL NEWS, 1899, vol. lxxix., pp. 99, 111), upheld the use of lime, and proposed, as a convenient though perhaps not quite so perfect substitute, sodium tungstate containing an excess of tungstic oxide. In this article they likewise indicate the precautions now used to ensure complete collection and retention of the boron. For a useful modification in the way of collecting the boric ether in ammonia before bringing in contact with the lime, see Penfield and Sperry (*Amer. Journ. Sci.*, 1887, Third Series, vol. xxxiv., p. 222); also Moissan (*Comptes Rendus*, 1893, vol. cxvi., p. 1087, and *Bull. Soc. Chim.*, 1894, vol. xii., p. 955), who modifies the Gooch distilling apparatus in certain respects.

chloride or sulphate, or even as free ammonia, was given off on heating. Its appearance was not limited to one or a few specimens of a series, but seemed to be characteristic of all, and to be afforded by the unbroken rock as well as by the powdered sample. The precise conditions under which the specimens were collected not being known, it is impossible to affirm positively that the ammonia may not have been due to recent organic contamination of some sort, especially in the case of the slates, but it is believed that a more critical collection of material will not alter the general result. Its amount was sometimes readily determinable by Nesslerisation, being as high as 0·04 per cent in some slates. Carbonaceous organic matter was absent from most of these, but doubtless existed in them in their early history. In their case the ammonia was, in part at least, evolved as such, imparting a strong alkaline reaction to the water in the upper part of the tube. The presence of sulphides, fluorides, or chlorides in the rock might cause the ammonia to appear as a sublimate of sulphate, fluoride, or chloride. Speculation on this matter would be altogether premature, but attention is called to it in the hope that other observers may be led to look for and investigate similar appearances. It should be borne in mind that the nitrogen present would not necessarily appear as ammonia or ammonium salts, since it might be given off in the elemental condition, as with the gases obtained from uraninite.

XXVII. *Special Operations.*

The problem often presents itself of ascertaining the composition of that portion of a rock powder which is soluble in special reagents or in a reagent of a particular concentration. No precise directions can be formulated to meet such cases. The procedure must vary with the character of the constituents of the rock, and with the object which it is sought to attain, and only in exceptional cases can a separation of this kind be sharp. Much depends on the degree of fineness of the powder, and on the length of time it is exposed to the action of the reagent.

Detection of Nepheline in presence of Olivine.

For confirmation of the microscopic diagnosis, Prof. L. V. Pirsson (*Amer. Journ. Sci.*, 1896, Fourth Series, vol. ii., p. 142), has indicated a means of detecting nepheline in presence of olivine, as in nepheline basalts, based on the very ready solubility of nepheline, as compared with olivine, when boiled for but one minute with a sufficiency of very dilute nitric acid (1:40). Gelatinisation of the filtrate on evaporation is taken as evidence of the presence of nepheline. If olivine is present in quantity, however, this test must not be accepted at once as final, for some, if not all, olivines are much more soluble in nitric acid of the above strength than Professor Pirsson was led to believe from his original tests. If, therefore, on evaporation of the filtrate, much iron is indicated, the gelatinisation may well be due to olivine alone or in part, and then the quantitative relation of silica to iron plus magnesium should be ascertained. It must also be borne in mind that any other very soluble silicates present will be more or less affected, and that apatite is largely or wholly dissolved. It is possible that still more dilute nitric, or perhaps some other, acid may exert a slighter solvent action on olivine without being appreciably less effective in dissolving nepheline, &c. In combination with a quantitative analysis of the extract the method is perhaps susceptible of a wider application than the particular case for which it was first used. It is well worth further study.

Estimation of Soluble Silica.

Very often in treatment by acids silica is separated in gelatinous or granular form mixed with the unattacked minerals, and it becomes necessary to remove or estimate this silica, or else to discriminate between soluble and insoluble silica already existing together. Usually a boiling solution of sodium carbonate has been employed for this purpose, though the caustic alkalis have found advocates. Lunge and Millberg (*Zeit. fur Angewandte Chem.*, 1897, pp. 393, 425), have lately conclusively shown that quartz is not nearly so insoluble in solutions of the caustic alkalis as has been supposed, but that, given a sufficient degree of subdivision, it can be brought wholly into solution; that it is impossible to secure correct separation of quartz and opaline silica by the use of either caustic or carbonated alkalis; and that digestion on the water-bath for fifteen minutes with 5 per cent solution of sodium carbonate is the only way to secure exact separation of unignited precipitated silica from quartz, and then only when the finest flour has been removed by levigation. The authors say:—

If, however, no more of such flour is present than is produced in the ordinary operations of powdering and sifting through cloth of the finest mesh, the error arising from the above mentioned treatment is so slight that it can generally be neglected; it reaches 0·1 to at the most 0·2 per cent of the total silica, by which amount the quartz will appear too low, the amorphous silica too high.

The above authors also show, however, that the solvent action of the caustic alkalis on quartz becomes very apparent only when the material has been reduced to such an utterly impalpable degree of fineness as is practically never reached in the preparation of samples for rock analysis. For this reason I have no hesitation in recommending the employment of a dilute solution of sodium hydroxide when the silica separated by acid from one of several mineral constituents of a rock is to be estimated. Even when dilution is considerable, solution is almost immediate, and as soon as this is accomplished—the point being known by the change in appearance of the residue—the solution should be diluted with cold water, and filtered at once. The difficulty met with in filtration may often be overcome by faintly acidifying, which has the added advantage of at once arresting any further action of the alkali. If the dilution is sufficient no separation of silica results from so doing. Very dilute acid should also be used for washing. Lunge, when using sodium carbonate, washes with hot carbonate solution to which alcohol has been added, thus obtaining clear filtrates.

XXVIII. *Estimation of Minute Traces of certain Constituents.*

If, as sometimes may happen, the problem is presented of examining rocks for traces of gold, silver, and other elements which are not ordinarily looked for, as in Sandberger's investigations bearing on the origin of the metalliferous contents of veins, large weights of material must be taken, up to 50 grms. or more. This involves the use, also, of large quantities of reagents, the purity of which must then be looked to with the utmost care. Special directions to meet such cases can not now be given, nor even a complete reference list of the scanty and scattered literature on this subject. Sandberger's own writings deal but little with its analytical side, and from its inaccessibility in the Washington libraries the writer is as yet unacquainted with the report by Von Foullon, "Ueber den Gang und die Ausführung der Chemischen Untersuchung." (*Jahrbuch der Bergakademie, Leoben u. Pribram*, 1887, p. 363), following Sandberger's own paper in the general report, "Untersuchungen der Nebengesteine der Pribramer Gänge."

(From Sandberger's report it appears that the rocks were treated successively with water, acetic acid, boiling dilute hydrochloric acid for two days, and finally hydrofluoric acid, the several extracts, and final residue of fluorides, and pyrite, being separately examined for heavy metals. The products of distillation were also examined. A striking fact observed in all cases was the complete insolubility of the pyrite, even after the severe treatment mentioned. This speaks strongly in favour of the correctness of ferrous iron estimations in silicates by the hydrofluoric and sulphuric acid method when pyrite is present unaccompanied by other sulphides). (See p. 220).

The present writer has published a few data as to gold,

silver, lead, zinc, &c. (*Mon. U.S. Geol. Survey*, 1886, Appendix B. vol. xii., pp. 592—596), in Mr. S. F. Emmons's report on "The Geology and Mining Industry of Leadville"; and Mr. J. S. Curtis (*Mon. U.S. Geol. Survey*, 1884, vol. viii., pp. 120—138), in his report on "The Silver-Lead Deposits of Eureka, Neveda," has given his method of assaying rocks for traces of gold and silver.

To Prof. F. W. Clarke and Dr. H. N. Stokes the writer's thanks are due for friendly suggestions in the preparation of the foregoing work.

ON THE RESULTS OF A SEARCH FOR OTHER SUGARS THAN XYLOSE AND DEXTROSE IN THE PRODUCTS OF THE HYDROLYSIS OF WOOD FROM THE TRUNKS OF TREES.*

By F. H. STORER, Professor of Agricultural Chemistry.

(Continued from p. 250).

B. *Acid Hydrolysis of Wood from the Root of a Sugar Maple Tree.*—A root, from an inch to an inch and a half in thickness, was dug up in November at West Newfield, Maine. The bark was stripped off, and the wood ground to powder. A quantity of the powdered wood was soaked in strong ammonia water during twenty-four hours, and then thrown upon a filter, and washed with water. The wood thus leached with ammonia was dried at 100°, and subjected to hydrolysis as follows:—Seven grms. of the dry residue were boiled for three hours in 200 c.c. of hydrochloric acid of 3 per cent, and the undissolved residue was separated by filtration. One half of the liquid was neutralised with sodium hydroxide, evaporated, and decolorised with bone-black. It gave quasi-$[\alpha]_D = 59{\cdot}26°$, and there was shown by Fehling's liquor 23·04 per cent of "sugar" (calculated as dextrose) in the dry root wood that had been leached with ammonia.

The other half of the acid filtrate was boiled three hours longer, and then neutralised with sodium hydroxide, and decolorised with bone-black. The approximate specific rotation in this case was quasi-$[\alpha]_D = 68{\cdot}21°$, and the "dextrose" shown by Fehling's liquor was equal to 16·30 per cent of the dry wood that had been leached with ammonia.

Both the higher rotation observed in these two trials of root wood and the larger percentage of dextrose, as compared with the corresponding experiments with trunk wood, are explained by the fact that the wood of the maple root contained much more starch than the trunk wood did. While the latter was well nigh absolutely devoid of starch, the root wood, when tested with barley malt, showed as much as from 5 to 7 per cent of "starch and sugar," *i.e.*, matters capable of reducing copper from Fehling's liquor. Indeed, on merely boiling some of the powdered root with successive portions of water, enough reducing matter was dissolved to indicate 4·12 per cent of sugar ("dextrose") when tested with Fehling's liquor, while the trunk wood gave no indication of starch when thus tested. Under the microscope also much more starch was found in the root wood than in the trunk wood. (See *Note*). All of which consists with the view, not infrequently enunciated, that appreciable quantities of starch are stored in the winter in the roots of trees.

(NOTE.—My colleague, Mr. E. W. Morse, who was good enough to examine specimens, noticed much blue colouration on testing the maple root wood with iodine, although he obtained no reaction for starch, either in the outer or inner wood, or in the bark of the trunk of a maple tree that had been felled on May 1st. A hardly visible reaction with iodine was got, along the medullary rays, on testing the outer and inner wood of a maple tree felled on May 30th. On examining wood and bark from the trunk of a sugar maple tree, felled in October, he got no reaction for starch in the bark; and the outer wood gave the starch reaction only in the medullary rays, excepting a few cases where scattering starch grains were detected in the wood fibre, usually not far from the medullary rays. Some starch grains were observed in the medullary rays of the inner wood also, but they were few in number, *i.e.*, they were still less numerous than those observed in the outer wood of the same tree. Pith from a stem of an elder bush (*Sambucus*) cut in July gave no reaction with iodine. Wood cut from the stem of a red maple tree in June gave a decided reaction along the medullary rays, while wood cut on the same day from a grey birch tree showed only a slight colouration with iodine; indeed, there were so few of the blue coloured granules lying in the medullary rays that they could readily be counted).

As was the case in the experiment described on page 249, so here, the long continued boiling appeared to have produced reversion (or destruction?) of a part of the dextrose that had been formed at first. On mixing what remained of the two solutions from the hydrolysis with 3 per cent hydrochloric acid, they were evaporated nearly to dryness, and the residue was treated with strong alcohol. The matter insoluble in alcohol gave quasi-$[\alpha]_D = 84{\cdot}69°$, and the matter soluble in alcohol gave quasi-$[\alpha]_D = 39{\cdot}41$.

The residual wood left after hydrolysing with hydrochloric acid of 3 per cent was soaked in 80 c.c. of strong hydrochloric acid of 35 per cent during twenty-four hours in the cold, and the mixture was poured into enough boiling water to dilute the acid to a strength of 3 per cent. The diluted mixture was boiled during three hours, and then filtered. One half the filtrate, neutralised with sodium hydroxide, evaporated, and decolorised with bone-black, gave quasi-$[\alpha]_D = 76{\cdot}78°$, and "dextrose" to the amount of 7·33 per cent of the dry material operated upon, or to 5·64 per cent of the dry wood that had been leached with ammonia.

The other half of the acid filtrate, after having been boiled three hours longer, gave anomalous results, as to rotatory power, while Fehling's liquor showed only 2·94 per cent of "dextrose" calculated on the dry wood that had been leached with ammonia. To all appearance much of the sugar produced in the first hydrolysis had been destroyed by the second boiling.

The residual wood, from the foregoing hydrolysis with strong hydrochloric acid, was treated with 10 c.c. of concentrated sulphuric acid (of 92·5 per cent of H_2SO_4), and left to stand in the cold during twenty-four hours. It was then poured into enough boiling water to bring the mixture to a strength of 3 per cent H_2SO_4, and the whole was boiled for three hours. The filtered liquid was divided into two parts. One part was neutralised with calcium carbonate, and evaporated. It did not need to be decolorised. The solution gave quasi-$[\alpha]_D = 73{\cdot}48°$, and "sugar" enough to amount to 32·12 per cent of dextrose in the dry matter operated upon, or to 29·91 per cent in the dry wood that had been leached with ammonia.

The rest of the neutralised solution was evaporated to dryness, and the residue was treated with hot, strong alcohol. The light brown, sticky mass insoluble in alcohol did not need to be decolorised when taken up with water. It gave quasi-$[\alpha]_D = 79{\cdot}34°$, and Fehling's liquor indicated 19·29 per cent of sugar calculated as dextrose on the dry wood that had been leached with ammonia.

The matter soluble in alcohol, on being dissolved in water, after the expulsion of the alcohol, gave quasi-$[\alpha]_D = 54{\cdot}60°$, and Fehling's liquor showed dextrose enough to amount to 13·93 per cent of the dry wood that had been leached with ammonia.

The second portion of the acid filtrate from the hydrolysis with 3 per cent sulphuric acid (after the action of strong sulphuric acid) was boiled three hours longer, after it had been removed from the wood. It was then neutralised with calcium carbonate, and evaporated. The

* *Bulletin of the Bussey Institution*, 1900, vol. ii., Part 9.

solution did not need to be decolorised. It gave quasi-$[\alpha]_D = 68{\cdot}58°$, and Fehling's liquor showed 33·16 per cent of "dextrose" calculated on the dry substance operated upon. On being again evaporated, it was treated with hot, strong alcohol. The matter insoluble in alcohol on being dissolved in water gave quasi-$[\alpha]_D = 58{\cdot}33°$, and Fehling's liquor showed 22·92 per cent of "dextrose." The matter soluble in alcohol gave quasi-$[\alpha]_D = 66{\cdot}30°$, and Fehling's liquor showed 9·45 per cent of dextrose.

It will be noticed that, as indicated by Fehling's test, the total amount of sugar obtained from the three prime hydrolyses of the maple root was by no means inconsiderable. After the first action of the 3 per cent hydrochloric acid on the wood that had been leached with ammonia the tests indicated 23·04 per cent of sugar; after the second action (3 per cent HCl, after soaking in strong, cold HCl), the tests showed 5·64 per cent, and after the treatment with strong sulphuric acid they showed 23 per cent. That is to say, the indications were that nearly 52 per cent of sugar, all told, had been got from the root wood which had been leached with ammonia, and dried at 100°.

In the case of the trunk wood the tests showed, respectively, 16·21 per cent, 3·17 per cent, and 27·04 per cent of "dextrose." In all 46·42 per cent of the dry wood. These figures (as indicated by Fehling's liquor) depend of course solely on the presumption that the observed reductions were due to the presence of sugars properly so-called. As will be shown directly, this presumption is not justifiable; but at this stage of the investigation it was regarded as a not wholly improbable hypothesis, and many efforts were made to isolate in visible, tangible form the substance whatever it might be that exhibited a rotatory power higher than dextrose. For example, rather more than 50 grms. of powdered maple root were boiled over a free flame in a flask with reflux condenser for three hours with 1000 c.c. of dilute sulphuric acid (of 3·5 per cent) to remove starch and some of the xylan. The filtrate obtained in this way was neutralised with calcium carbonate, evaporated, and examined. It showed quasi-$[\alpha]_D = 47{\cdot}87°$, and "dextrose" (in some part xylose), enough to amount to 14·35 per cent of the dry wood.

The undissolved residue from this first treatment was left over night to dry out somewhat in the air, and 30 c.c. of strong sulphuric acid, of 90 per cent H_2SO_4, were added to it. The mixture was left to itself during twenty-four hours, and was then poured into enough boiling water to reduce the acid to the strength of 3·5 per cent. After this dilution the mixture was boiled over a free flame for three hours, and the filtrate was set aside to be added to the product of the next hydrolysis.

In this particular instance the treatment with strong sulphuric acid was not wholly satisfactory, because in the course of it evidence presented itself that the residue from the treatment with 3·5 per cent acid had not been adequately dried. It had, in fact, retained so much moisture that the strong acid added to it was at once diluted to such an extent that it had no proper opportunity to act upon the cellulose in the wood. It was noticed, for example, that even 30 c.c. of the strong acid made a pasty mass with the residue, and that only a small part of the residue was blackened. Hence, the residue from this treatment with strong acid was dried carefully, and again mixed with a new portion of the strong sulphuric acid. In this case the residue blackened instantly and throughout when the strong acid was added to it, and 70 c.c. of the acid were required to bring about the desired pasty condition.

After standing during twenty-four hours the mixture was poured into enough boiling water to reduce the acid to the strength of 3·5 per cent, and boiled over a free flame for three hours. The filtrate from this treatment was added to that previously obtained, as above stated, after the first application of the strong acid, calcium carbonate was added to neutralise the acidity, and the filtered liquid was evaporated to a syrupy condition. After decolorising with bone-black, this solut on showed quasi-$[\alpha]_D = 63{\cdot}42°$, and "sugar" enough to amount to 9·65 per cent of the dry wood.

It is worthy of remark that in this trial where 50 grms. of wood were boiled directly in an acid of 3·5 per cent, and the residue was treated with sulphuric acid of 90 per cent H_2SO_4, and where a 3·5 per cent acid was used again in the final hydrolysis, less sugar (14·35+9·65=24 per cent) was obtained than had been got previously where a smaller quantity of wood (10 grms.), a slightly weaker dilute acid (3 per cent), and a more concentrated strong acid (92·5 per cent H_2SO_4) were employed; for in that case the yield of "sugar" was 23·04 + 5·64 + 23 = nearly 52 per cent. So, too, in subsequent trials, less sugar was got from 50 grm. portions of wood after treatment with acid of 90 per cent than had been got in the earlier trials.

In respect to the action of strong sulphuric acid, it may here be said that (after the wood had soaked in strong acid), the 10 grm. portions were boiled in 464 c.c. of acid of 3·5 per cent, while the 50 grms. portion were boiled in 3250 c.c. of acid of 3 per cent.

Another difference of treatment in the two particular instances above cited was that the 10 grm. portion had been leached first of all with ammonia, then boiled with dilute hydrochloric acid, and afterwards soaked in strong hydrochloric acid, and again boiled in this acid, after dilution, before they were soaked in strong sulphuric acid; while neither ammonia nor hydrochloric acid were used upon the 50 grm. portions of wood. Here the powdered wood was boiled at once in dilute sulphuric acid of 3·5 per cent, and afterwards soaked in the strong sulphuric acid of 90 per cent, and again boiled, after dilution to 3·5 per cent.

In the hope of obtaining crystals 15 grms. of the thick syrup, left on evaporating the neutralised liquor from the hydrolysis by dilute acid after treatment with strong sulphuric acid, were warmed in a dish together with 10 c.c. of water, and 20 c.c. of strong alcohol were added. After three days it was found that a slimy mass had settled at the bottom of the dish. Sixty c.c. of strong alcohol were poured upon it, and the dish was left to itself in an exsiccator. No perceptible change occurred in the course of a fortnight; the clear brown solution was then filtered off, and the stringy, brown residue was washed with a little dilute alcohol. It became white under this treatment. On attempting to dry it on a watch-glass in an air-bath, it began to melt at 70°; when it was immediately taken from the bath, and set aside in an exsiccator. Next morning the contents of the watch-glass were found to be solid, and numerous needle-like crystals were visible upon and in the midst of the mass. Under the microscope the crystals were well defined, and it could be seen that many of them had pyramidal terminations. After a time these crystals effloresced in dry air. The whole of the crystalline mass was tested for mucic acid by treating it with nitric acid of 1·15 sp. gr. It was oxidised completely by this acid, and a clear solution was obtained from which after a while a white powder was deposited. This precipitate was so white and of such excellent appearance that the treatment with ammonium carbonate, ordinarily employed for separating mucic acid from insoluble contaminations, was omitted, and the precipitate was collected directly, and weighed. Dried at 100°it amounted to 11·36 per cent of the weight of the crystalline mass, supposed to contain sugar, which had been subjected to the action of the nitric acid; on examination, however, the precipitate turned out to be not mucic acid, but mere inorganic matter. On dissolving it in ammonium carbonate, evaporating to dryness, and treating anew with nitric acid, only a very small precipitate appeared, and this also was found to consist wholly of inorganic matter, the source of which will be suggested later on.

In order to determine whether the matter insoluble in alcohol, obtained as above, is always contaminated with inorganic substances, another portion of the powdered maple root (more than 50 grms.) was hydrolysed as before;

first with dilute sulphuric acid of 3·5 per cent, to remove starch and xylan, and subsequently after treatment with strong sulphuric acid of 90 per cent H_2SO_4, with acid that had been diluted to 3·5 per cent. In the treatment of this sample care was taken to dry thoroughly the residual cellulose left after the action of the first acid of 3·5 per cent, before adding to it 70 c.c. of strong sulphuric acid. This strong acid was left in contact with the cellulose during twenty-four hours, and was then diluted to 3·5 per cent, and boiled and examined as before.

In this instance the liquor obtained from the first hydrolysis was 3·5 per cent acid, and supposed to contain a mixture of xylose and dextrose, showed quasi-$[\alpha]_D = 42·87°$, and enough "sugar" to amount to 15·48 per cent dextrose, calculated on the dry wood. On the other hand, the product of the hydrolysis after the action of strong sulphuric acid gave quasi-$[\alpha]_D = 63·75°$, and "sugar" enough to amount to 1·07 per cent of the dry wood.

The syrup left on evaporating most of the liquor from the hydrolysis after the strong acid was a brown molasses. Strong alcohol was added to it in three successive portions, the last portion being left over night in contact with the insoluble matter. This precipitate, which was lighter coloured than the syrup from which it came, was dissolved in a very small quantity of water, and heated carefully upon an oil-bath to 65° C., and then set aside in a desiccator to cool. After twenty-four hours the dish was found to contain a solid crystalline mass, in and upon which, as in the previous instance, were to be seen numerous acicular crystals. Under the microscope these needles seemed to be hexagonal prisms, many of which had well-defined terminations. After a day or two these crystals effloresced in dry air, while preserving their original shape. They were found to consist for the most part of inorganic matter.

The solution obtained on dissolving this crystalline mass in water showed no disposition to form a syrup on being evaporated. On the contrary, it left a dark brown, somewhat granular residue, which remained unchanged in appearance on the addition of strong alcohol. After driving off the alcohol, dissolving in water, decolorising with bone-black, and again evaporating to dryness, a very small quantity of water was added, the mixture was heated to 60°, and set aside in an exsiccator; it dried out to a solid mass in which no crystals were visible. Six weeks later, on treating the dry residue with alcohol of 75 per cent, a very small portion of it dissolved; but most of it dissolved in alcohol of 60 per cent. The alcohol solutions, mixed one with the other, showed no indications of crystallising, but dried down to an amorphous mass which was taken up with four-fifths its weight of water. On adding to this solution twice its volume of alcohol of 93 per cent, an apparently gelatinous precipitate began to form, and increased on standing. This precipitate was found to consist of fine crystals of inorganic matter. Moreover, the residue which was left undissolved at the time of treating with alcohol of 60 per cent was seen to consist of white crystals of inorganic matter.

For the moment it was a matter of uncertainty whether this inorganic matter consisted merely of ash-ingredients proper to the wood, or whether it might not have been derived from acids, produced in the process of hydrolysis, that were capable of forming soluble calcium salts. In the hope of avoiding the inorganic substances which had thus far contaminated the "matter insoluble in alcohol," various experiments were now made with carbonic acid; and with lead carbonate as the neutralising agent, instead of calcium carbonate or barium hydroxide, and with cotton also instead of wood. For the conclusions to be drawn from the results of these trials, see *prox.*

The unusually small quantity of sugar (1·07 per cent) obtained in the experiment, described above, led to a repetition of it.

Some 54 grms. of powdered maple root were boiled for three hours in 1000 c.c. of dilute sulphuric acid of 3·5 per cent, to get rid of xylan and starch; the residue was dried in the air, and treated with 70 c.c. of strong sulphuric acid of 90 per cent H_2SO_4, then poured into 3247 c.c. of boiling water to reduce the acid to a strength of 3·5 per cent, and boiled for three hours. The filtrate was neutralised with calcium carbonate, and, after the precipitated calcium sulphate had been removed by filtration, carbonic acid gas was passed into the clear liquor, which was subsequently boiled. The slight precipitate which formed was filtered off, and the liquid was evaporated to the bulk of 428 c.c. It did not need to be decolorised. It gave quasi-$[\alpha]_D = 79·89°$, and 13·61 per cent dextrose, calculated on the dry root wood. On being evaporated to dryness and treated with strong alcohol, a large portion of the residue failed to dissolve.

In still another experiment rather more than 50 grms. of powdered maple root were boiled for three hours in 1000 c.c. of 3·5 per cent sulphuric acid; the undissolved wood was filtered off, dried thoroughly, and left to soak during twenty-four hours with 70 c.c. of sulphuric acid of 90 per cent H_2SO_4. The mixture was poured into 3250 c.c. of boiling water, and the boiling was continued during three hours. The filtrate was neutralised with lead carbonate, and, after the removal of the lead sulphate, sulphuretted hydrogen was passed through the filtrate to remove any lead which might be held in solution. After removing the lead sulphide and the excess of sulphuretted hydrogen, the solution tested with Fehling's liquor showed 0·84 per cent of dextrose, calculated on the dry wood, and gave quasi-$[\alpha]_D = 82·15°$. The low percentage of dextrose is remarkable.

(To be continued).

THE SULPHOCYANIDES OF COPPER AND SILVER IN GRAVIMETRIC ANALYSIS.

By R. G. VAN NAME.

Cuprous Sulphocyanide.

As early as 1854 attention was drawn by Rivot (*Comptes Rendus*, xxxviii., 868) to the possibility of estimating copper gravimetrically by weighing as cuprous sulphocyanide, and to the advantages which the process afforded in separating copper from other metals. Rivot's method of procedure consisted in dissolving the substance to be analysed in hydrochloric acid, reducing the copper with hypophosphorous or sulphurous acid, and precipitating with potassium sulphocyanide. The precipitate dried at a moderate temperature was weighed as cuprous sulphocyanide and then as a control converted by ignition with sulphur into cuprous sulphide and weighed in that condition.

In his well-known work upon Quantitative Analysis Fresenius in one place (6th Aufl., i., 187) denies the practicability of the direct weighing of copper as cuprous sulphocyanide on account of the tendency of the latter to hold water even when heated to the temperature of incipient decomposition. As authority for this statement he cites Claus (Gmelin's "Handbook," iv., 472), who found 3 per cent of water in the precipitate after drying at 115°, and Meitzendorff, who gave the percentage of water under the same conditions as 1·54.

On a later page of the same volume, however (6th Aufl., i., p. 335), Fresenius, after a trial of the process which gave 99·66 per cent of the theory for copper, concludes that the method is practicable although apt to give low results, particularly in the presence of free acid.

The process was again recommended in 1878 by Busse (*Zeit. Anal. Chem.*, xvii., 53), who had employed it for the estimation of copper, both alone and in the presence of iron, nickel, zinc, and arsenic, obtaining results very near the theory and plainly comparable with the figures ob-

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. x., p. 451.

TABLE I.

25 c.m.³ of N/10 $CuSO_4$ solution, equivalent to 0·0795 grm. Cu, taken for each experiment.

	H_2SO_4 concentrated.	HNH_4SO_3 sat. sol.	NH_4SCN approx. N/10.	Final volume.	Time of standing.	Cu found.	Error.
	C.m.³.	C.m.³.	C.m.³.	C.m.³.	Hours.	Grm.	Grm.
1.	None	5	13	68	½	0·0795	0·0000
2.	None	3	13	66	48	0·0793	−0·0002
3.	None	3	25	78	½	0·0796	+0·0001
4.	None	3	25	78	12	0·0796	+0·0001
5.	1·5	10	13	85	12	0·0792	−0·0003
6.	1·5	8	13	105	48	0·0785	−0·0010
7.	1·5	3	25	85	4	0·0783	−0·0012
8.	1·5	5	25	85	21	0·0795	0·0000
9.	5	5	25	85	3	0·0797	+0·0002
10.	15	10	25	115	21	0·0793	−0·0002
	HCl concentrated.						
11.	10	5	25	100	20	0·0795	0·0000
12.	25	10	25	100	28	0·0784	−0·0011

TABLE II.

	Cu taken.	H_2SO_4 conc.	NH_4SCN approx. N/10.	Final volume.	$Cu_2S_2(CN)_2$ found, calc. as Cu.	Error.	Cu in filtrate.
	Grm.	C.m.³.	C.m.³.	C.m.³.	Grm.	Grm.	
1.	0·3175	None	60	500	0·3176	+0·0001	None.
2.	0·3175	None	60	500	0·3177	+0·0002	None.
3.	0·3175	None	60	500	0·3176	+0·0001	None.
4.	0·3175	10	100	500	0·3175	0·0000	None.
	HCl conc.						
5.	0·3175	20	100	500	0·3165	−0·0010	Distinct.

TABLE III.

Final volume of liquid, 150 c.m.³. 25 c.m.³ of NH_4SCN solution equivalent to 25·15 c.m.³ of $AgNO_3$ solution.

	NH_4SCN.	$AgNO_3$.	Excess of $AgNO_3$.	AgSCN found.
	C.m.³.	C.m.³.	C.m.³.	Grm.
1.	25	25·3	0·15	0·4372
2.	25	25·3	0·15	0·4376
3.	25	25·4	0·25	0·4373
4.	25	25·4	0·25	0·4375
5.	25	30·4	5·25	0·4382
6.	23	Rough excess.		0·4366
7.	25	,,	,,	0·4381
8.	25	,,	,,	0·4373
9.	25	,,	,,	0·4372
10.	25	,,	,,	0·4369

TABLE IV.

	AgSCN taken.	Calc. as Ag.	Ag found by battery.	Error.	Weighed as AgCl.	Calc. as Ag.	Error.
	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
4.	0·4375	0·2844	0·2839	−0·0005	0·3765	0·2834	−0·0010
10.	0·4369	0·2840	0·2838	−0·0002	0·3761	0·2831	−0·0009

tained by afterwards igniting the cuprous sulphocyanide with sulphur in hydrogen.

In spite of the evident advantages for certain purposes of Rivot's method over other modes of determining copper, it has never come into general use. The chief reason for this has apparently been the difficulty and inaccuracy attendant upon the weighing of the precipitate upon dried paper filters, a process which can hardly be depended upon unless managed with extreme care.

In the experiments to be described this difficulty was avoided by performing the filtering and weighing upon asbestos in a perforated platinum crucible. The method of conducting a determination was as follows:—A suitable quantity of a standard copper sulphate solution was run from a burette, diluted to a convenient volume, a few cubic centimetres of a saturated solution of ammonium bisulphite added, and the copper precipitated by an excess of ammonium sulphocyanide. The precipitate was allowed to settle, collected upon asbestos in a weighed crucible, washed with cold water, and dried at 110° until no further loss of weight took place.

In Table I. are given the results of a number of determinations made in this way. The copper sulphate solution was made up exactly decinormal, and the standard confirmed electrolytically. As the ammonium sulphocyanide solution was slightly above decinormal, 13 c.m.³ represent a small excess (about 1 c.c.) above the amount theoretically required to precipitate 25 c.m.³ of the copper sulphate solution. The ammonium bisulphite, which had been recently prepared by saturating aqueous ammonia with sulphur dioxide, was always used in sufficient quantity to give the liquid a strong and permanent odour of the latter.

When there is no free acid present the time of standing

before filtration and the amount of the excess of ammonium sulphocyanide are practically without effect, as experiments 1 to 4 of the table show.

Experiments 5 to 10 were carried out in the presence of various amounts of free sulphuric acid up to 12 per cent of the total volume of liquid. The acid, at least within this limit, does not exert a sufficient solvent effect upon the cuprous sulphocyanide to interfere materially with the accuracy of the process, but it retards the precipitation, making it necessary to increase the time of standing before filtering in proportion to the amount of acid present. In several of these determinations the precipitation was visibly incomplete even after several hours standing. This effect of the acid, however, hardly shows in the results of the table, because the standing was always prolonged until the copper appeared to be all down before filtering.

The low results of No. 7 was probably due chiefly to incomplete precipitation, although No. 9 shows that even with a much larger amount of acid precipitation may be complete within three hours. In general, however, it is safer to allow ample time (twelve hours or more) for the precipitation when there is much free acid present.

Comparison of Nos. 5 and 6, for which only a bare excess of ammonium sulphocyanide was used, with Nos. 7 to 12 shows an apparent advantage in the larger excess in the presence of acid. Hydrochloric acid, judging from the results of Nos. 11 and 12, has no greater disturbing influence than sulphuric acid, although in No. 12, where the concentrated acid constituted one-fourth of the entire volume, there was apparently a slight solvent action. The filtrate from this determination when concentrated to about 25 c.m.³ and treated with potassium ferrocyanide gave a strong test for copper, as did also the filtrate from No. 6. Several of the other filtrates were tested in the same way, but none showed more than an insignificant trace of copper. No. 7, however, was not tested.

Table II. contains the results of a series of experiments conducted as before, except that larger amounts of copper were employed. The copper sulphate solution was approximately N/5 and standardised by the battery. The solution of ammonium sulphocyanide was the same previously used, and a considerable excess was employed in every determination. More than twice the amount theoretically required was used in every case where free acid was present, and at least twenty hours were allowed for the precipitation, which was made in cold, and, as the table shows, rather dilute solutions. If the solution is too concentrated the copper is apt to be thrown down in a finely divided condition, making it hard to filter.

The time required to dry the cuprous sulphocyanide at 110° is in general from two to three hours. Heating much longer than this is not to be recommended, as a gradual increase in weight begins to take place, as is shown by the following example, which gives a series of weights of the same precipitate at different stages.

	$Cu_2S_2(CN)_2$ Grm.	Calculated as Cu. Grm.
After 2 hours at 110° ..	0·6060	0·3167
,, 4 ,, ,, ..	0·6059	0·3167
,, 19 ,, ,, ..	0·6067	0·3171
,, 23 ,, ,, ..	0·6069	0·3172

This tendency to increase in weight is, however, usually less marked than in the above example, and in any case need not interfere materially with the accuracy of the process unless the drying is prolonged far beyond the necessary length of time.

The method is easily handled, and as the results of Tables I. and II. show, is capable of considerable accuracy. From the nature of the process it is evident that it is much less likely to be interfered with by the presence of other metals than the other gravimetric methods for copper, and may therefore be directly applied with good results in many cases where the use of the electrolytic or the oxide method would involve a previous separation.

Silver Sulphocyanide.

The sulphocyanide of silver, unlike that of copper, is soluble in an excess of ammonium or alkali sulphocyanides, and this fact prevents the use of the latter to precipitate silver for gravimetric estimation. The reverse process, however, the precipitation of a soluble sulphocyanide by an excess of silver nitrate, as will be shown by the experiments to be described, furnishes a convenient means of standardising sulphocyanide solutions and in general for estimating thiocyanic acid.

When freshly precipitated the sulphocyanide of silver resembles the chloride in appearance, but when allowed to stand a few hours becomes finely granular and is very easily filtered and washed. It may be safely dried to a constant weight upon an asbestos filter at 110°—120°, but at a somewhat higher temperature is decomposed, leaving a residue of silver sulphide.

The determinations which are shown in Table III. were made as follows:—Portions of 25 c.m.³ of an approximately decinormal solution of ammonium sulphocyanide were measured from a burette, diluted with 100 c.m.³ of water, and silver nitrate added in excess. The precipitate was collected upon asbestos in a platinum crucible, washed with cold water, and dried to a constant weight at 115°; the drying requiring usually between two and three hours.

The filtering is facilitated by allowing a few hours for the precipitate to settle; but this is by no means essential, as it is easy with a little care to obtain a clear filtrate even when the filtering is performed at once.

The solution of ammonium sulphocyanide was prepared from a pure salt, especially tested and found free from chloride. This point is of importance, as chlorine is a common impurity and its presence in any considerable quantity will vitiate the results.

In order that the effect of varying the excess of silver might be investigated, an approximately decinormal solution of silver nitrate was titrated against the ammonium sulphocyanide and the ratio between the two solutions determined. This silver nitrate solution was used for the first five determinations of Table III. For the rest the quantity of silver nitrate was not measured but regulated by the eye alone, thus making the conditions the same as would be the case in practical use of the method.

These results are as uniform as could be expected, considering the variations which would be produced by even very small errors in measuring out 25 c.m.³ of decinormal sulphocyanide solution. It is, moreover, clearly shown that there is no difference in the results whether a bare excess or a moderately large excess of the silver nitrate is used.

The mean of the values in the last column is 0·4374, which is equivalent to 0·2006 grm. of ammonium sulphocyanide for every 25 c.m.³ of the solution.

The standard of the sulphocyanide solution was also determined volumetrically by Volhard's process. The mean of four titrations carried out with great care against a standard silver nitrate solution gave as the standard 0·2003 grm. of ammonium sulphocyanide for 25 c.m.³ of solution. This difference between the standards as determined by the two methods (1 part in 670) is much less than the variations which frequently appear between successive determinations by Volhard's method, under like conditions as to strength of solutions and amounts used. It is about equal to the error that would be produced in a single volumetric determination by a mistake of one drop in measuring one of the solutions, or of one-half drop in the same direction on each.

It is therefore evident that the standard of a sulphocyanide solution obtained in the above way may be applied directly to the estimation of unknown amounts of silver by Volhard's method without sensible error.

To remove a possible doubt as to whether the silver sulphocyanide dried at 115° was entirely free from water, a number of electrolytic determinations of the silver contained in the previously weighed precipitates of Table III. were made in the following way:—

The perforated platinum crucible containing the silver sulphocyanide and asbestos was hung in a loop of heavy platinum wire and served as the anode. For the cathode a deep platinum dish of about 200 c.m.³ capacity was used. An ammoniacal solution of potassium cyanide was employed as the electrolyte, and gave the best results when made up by dissolving 2 grms. of potassium cyanide in 15 c.m.³ of strong ammonia and 15 c.m.³ of water. The crucible which served as the anode was filled with this solution in full strength, and the remainder was put into the platinum dish and diluted to the required volume with water. In this medium the silver sulphocyanide is slowly dissolved and diffuses through the asbestos felt into the space between the electrodes, where the silver is deposited in the usual way. This diffusion is, however, aided but little, if at all, by the current, and there is a tendency for traces of the silver to remain behind in the crucible. The current density employed was about 0·0012 ampère per square centimetre of cathode surface and the time about twelve hours. After weighing the silver deposited, it was dissolved in nitric acid, precipitated by hydrochloric acid, and weighed again as the chloride, giving a check upon the results.

Seven of the ten determinations of Table III. were thus treated, but, owing to the imperfections of the process, the results were all slightly low, the worst showing a deficiency of 0·0025 grm. of silver—an error of less than 0·9 per cent. The results of the two best of these determinations (Table IV.), are, however, sufficient to prove the point in question—namely, that the silver sulphocyanide dried at 115° has the theoretical constitution and contains no water. The numbers are those under which the determinations appear in Table III.

It is clear, therefore, that the estimation of sulphocyanides by precipitation with silver nitrate and direct weighing of the precipitate is wholly permissible. The method is extremely simple, and, as has been shown, the results are quite accurate.

In conclusion, I wish to thank Prof. F. A. Gooch for many valuable suggestions given during the course of this investigation.

THE LITERATURE OF ALCHEMY.*

By HENRY CARRINGTON BOLTON.

The acquisition of riches surpassing the most extravagant dreams of avarice, the indefinite prolongation of life with perfect enjoyment of unfailing health both in body and mind, the attainment of a saint-like, unselfish spirit with hopes of a blessed immortality, were the unparalleled prizes promised by the pseudo-science of alchemy to those successful in penetrating its secrets; these and other less lofty allurements induced conscientious but misguided men to spend life-times, and to waste fortunes in search of the "Philosophers' Stone" capable of conferring such inimitable benefits. To gain the knowledge needed to secure this miraculous substance, two methods were open to students; first, to form the acquaintance of men claiming to possess the treasure, and to wrest from them the secret of its preparation, and secondly, to peruse the literature in which the mystery was believed to be hidden. The first plan necessitated long journeys, often to the little known and distant Orient, the wanderings extending to many years; the second required the accumulation of precious manuscripts and rare books, their careful study, and repetition in the laboratory of the processes obscurely described therein.

In the interiors of alchemists' laboratories painted by the Flemish artist Teniers, besides furnaces and crucibles, stillatories, and alembics, vellum covered handbooks and huge folios fitted with brass clasps are always conspicuous; the smaller volumes being held in the hand of the bearded alchemist, and the folios lying on the floor within reach. Teniers' studies are true to life, and one examining them in earnest longs to know what sort of literature was accessible to mediæval students of transmutation, what were its characteristics, who were their favourite authors, and what doctrines were propounded in the well-thumbed tomes.

Alchemical manuscripts and books are coeval with the pseudo-science that gave them birth, which has existed more than two thousand years. Or longer, if the claims of China be taken into account, as scholars tell us that the Chinese practised transmutation of metals full six hundred years before Europeans; indeed the Arabians are said to have acquired their knowledge by contact with Chinese merchants at Bagdad, an important Eastern market and early a centre of alchemical activity. The claims of China, moreover, are supported by finding the germs of a belief in transmutation in the religion of Tao, a sect founded by a contemporary of Confucius who died 478 B.C.

The early Chinese treatises on alchemy are written in an archaic style, with obsolete words, and many unknown characters that makes the task of deciphering them almost impossible for even expert sinologues. One of the earliest is entitled "Ts'an T'ung Ch'i," of which I own a reprint issued during the reign of the late Emperor Kuang Hsü (1873—93). A few years ago I made an effort to get this translated, at least in part, and had it examined by some of the first Chinese scholars of the world, but they abandoned the undertaking.*

Dr. Martin has, however, published notes on the treatise called the "Uniting Bond," written about the first century A.D. by a Tauist named Wei Peh Yang; this contains an account of an Elixir Vitæ having gold as its chief ingredient. "Gold is imperishable, fire does not injure its lustre; like the sun and the moon it is not affected by time, wherefore the Elixir is called the Golden (*Kin Tan*). Life can be lengthened by eating the herb *ku ma*, how much more by taking the Elixir which is the essence of gold, the most imperishable of all things. When partaken its influence will extend to the four limbs, the countenance will become joyful, white hair will turn black, new teeth will grow, and youthful vigour will replace the infirmities of age."

This passage reads like a glorified advertisement of the Keeley Gold Cure.

Alchemical books are still sold in the shops of Shanghai; one of the commoner is that entitled "Wu-chen-pien," in two volumes, written by Chang Pih Tuan about 1075 A.D.

Many of the alchemists were eminent scholars, but most of the ardent workers with furnaces and coals, lead, and mercury, were unlettered men who could not have profited by Chinese literature had it been available; all those seeking the "Way to Bliss," studied Latin translations of ancient Syriac, Arabic, and Greek manuscripts purporting to explain the preparation of the "Victorious Stone." These Latin versions were but fragmentary, they abounded in errors, glosses, and interpolations made by copyists, but their supposed antiquity and the renown of their reputed authors caused them to be most highly prized. Some of the genuine originals of these are still preserved in the great libraries of Europe, and are of curious interest to both the philologist and the historian of science; those in Syriac are translations from the Greek made in the seventh to the ninth centuries. The "Doctrine of Democritus" contains two treatises, "The Preparation of Gold," and "The Philosophers' Stone"; the latter deals with processes on metals, and on sulphur, arsenic, and ores, and is illustrated with rude sketches of chemical apparatus.

The first Mohammedan writer on alchemy was Prince Omeyyade, who died in 708; he was the teacher of Djâber,

* From the *Pharmaceutical Review*, vol xix., Nos. 4 and 5.

* It was seen by Dr. W. A. Martin, of Peking; Dr. John Fryer, then of Shanghai, who procured my copy for me; by Mr. Herbert Giles, of Aberdeen; by Miss Adèle Field, of New York; and by Lord Kingsgeast, of Tseng, of the Chinese Legation at London.

but only the titles of his works have come down to us. The Arabian physician Djâber, the Geber of the Latin authors, was the great master of the "sacred art," and enjoyed the highest reputation throughout the Middle Ages; he is credited with having written 500 treatises, an Oriental exaggeration. Those known exhibit evidence of Moslem faith, and as he himself admits, are written in an allegorical, obscure language; he shows familiarity with many mineral substances, and discourses on the changes in volume produced by heat and cold, but makes no reference to the mineral acids, nor to nitrate of silver, that Geber is supposed to have known. Perhaps the most satisfactory passage in his writings is the following from the "Book of Mercy":—

"I saw that persons engaged in attempts to manufacture gold and silver were working ignorantly and by wrong methods; I then perceived that they were divided into two categories, the dupers and the duped. I had pity for them both."

Berthelot, the distinguished French chemist who first collected the Arabic treatises, in 1893, made the discovery that the supposititious originals of many Latin works have no existence, the writers fraudulently claiming for the latter an Oriental origin; he showed that the chemical books attributed to the much lauded Geber are fictitious, and that the reverence paid to him as a pioneer in chemistry has been misplaced. Thus the whole history of chemistry has been falsified by giving credit to the Arabians for knowledge which really belonged to a period five hundred years later.

If we disregard the Egyptian papyrus named after Georg Ebers, which deals with the medical art, and dates back to 1550 B.C., the most ancient writings on alchemy are certain Greco-Egyptian papyri preserved in Leyden; several of them contain magical formulas, incantations, love philtres, and dream secrets, but one known as "Papyrus X" is a treasury of information on metallurgical operations at so early a period as the third century of the Christian Era. It was found in a tomb at Thebes, and may have been one of those ancient Egyptian books on the preparation of gold and silver which escaped the destruction ordered by the Emperor Diocletian in the year 290: an order issued lest the people using them should grow rich by their art, and revolt against the Romans.

This precious document contains more than one hundred recipes for making alloys to be used in the manufacture of cups, vases, images, and other objects of the goldsmith's art; also processes for soldering metals, and superficially colouring them, besides formulas for making gold and silver inks. The text is full of ignorant spellings and grammatical errors, which show the writings to have been the work of an uneducated artisan; the whole papyrus, in short, is evidently the memorandum book of a goldsmith (or silversmith), engaged in attempts to imitate gold and silver. This and similar MSS. prove that the doctrines of alchemy concerning the transmutation of metals did not originate in philosophical views of the constitution of matter, as generally supposed, but in the practical experiments of workmen trying to find fraudulent substitutes for the precious metals.

(To be continued).

NOTICES OF BOOKS.

Veterinary Posology. By GEORGE A. BANHAM, F.R.C.V.S. Second Edition. London: Baillière, Tindall, and Cox. 1901. Pp. 192.

THESE tables are intended as an aid to the memory for the dose and pharmacopœial preparations of the drugs used in veterinary medicine.

The author considers it more convenient to arrange the agents alphabetically instead of under various groups, and we quite agree with him that such an arrangement will save the busy practitioner a good deal of time.

The doses given in the three columns are for the horse, pig, and dog respectively; those for cattle, sheep, goats, and cats can easily be calculated from the former by means of a few factors which are given.

Amongst other tables which are included in this handy little volume we may call attention to the table of the General Classification of Medicines, according to their influence on the organs and structures of the body; the table of agents arranged according to their therapeutical action; the table of diseases and their remedies, &c. The book is supplied with a good index.

CORRESPONDENCE.

PROUT'S HYPOTHESIS AND RADIO-ACTIVE ELEMENTS.

To the Editor of the Chemical News.

SIR,—A writer to the CHEMICAL NEWS of March 22nd suggests that the discoveries of the heavy radio-active elements, all closely resembling formerly well known elements, may have the effect of reviving Prout's hypothesis that atomic weights should be expressed in whole numbers. He says that the presence of a small amount of a heavier element occurring as an unrecognised impurity might easily make enough difference in atomic weights to account for many of the small fractional variations from whole numbers. Atomic weight comparisons and theories have been popular with chemists for the past century, and as such comparisons led to the discovery of the periodic law they certainly cannot be regarded as valueless. Hence it may not be useless to follow out the ideas of the above-mentioned correspondent.

The past few years have been prolific in new elements, and in the promise of more; and in nearly all cases the new ones resemble closely other elements already well known. Lord Rayleigh and Professor Ramsay found a whole series of elements so much like nitrogen that they had previously escaped detection; and the recent spectrum investigations of Professors Liveing and Dewar indicate the existence of an indefinite number of other similar elements yet to be isolated. The new radio-active elements are so similar to bismuth, barium, and titanium that many chemists still hesitate to believe them different. Victorium, the latest of the rare earth group, is another instance of the same kind, as it so closely resembles others of the same group that it was isolated only by a most laborious method. The original yttrium, thought by Gadolin a century ago to be a single element, has proved to be the parent of a large number of children all bearing a family resemblance, and the possibilities of a further increase in the family seems almost unlimited.

There can be little doubt of the existence of a large number of undiscovered elements, and equally little doubt that many of them will be found very similar to elements now known—so similar that they may now exist unsuspected with the known elements, and may affect their atomic weights to the fractional extent that has seemed to disprove Prout's very convenient whole number hypothesis. According to the latest international table of atomic weights, published by the Commission of the Deutschen Chemischen Gesellschaft, taking O=16, there are 76 elements, 35 of which have their atomic weights expressed in whole numbers. Of the 41 others 16 vary from whole numbers by not more than 0·1. If these 16 could be added to the 35 it would give a list of 51, nearly 70 per cent of the whole number.

It can easily be seen that the admixture of a very small amount of a material of different atomic weight might easily account for the minor differences in the table. Let us take, for example, the first on the list, aluminium, with an atomic weight of 27·1. If this 0·1 be conceived as due to admixture of some unknown element it must of course

be heavier than the aluminium. If it be supposed to have an atomic weight of 28, it would constitute one-tenth of the element we now call aluminium. If the atomic weight were greater the proportion would be correspondingly less. The atomic weight of radium is reported to be about 174, not far from 36 higher than barium, which it so closely resembles. If the same difference be imagined in the case of aluminium, the new undiscovered element need be in the proportion of 1 to 359, an amount that might easily escape detection if it as closely resembled aluminium as radium does barium, or as argon does nitrogen.

The case of hydrogen is even more interesting. It is given an atomic weight in the table of 1·01, which is a little too high. It it be supposed to contain as an impurity an element having an atomic weight as great as helium—the next in the scale—the new element would have to be present in the proportion of 1 to 300, while if it were as heavy as neon it would be there as 1 to 1900.

Of course it is not very probable that a sufficient number of these conveniently located elements will be discovered, and so it is hardly likely that the atomic weights will be corrected in this way. Still it can easily be seen from the above facts that such is within the range of possibility, if not of probability.—I am, &c.,

EDWARD BOOTH.

University of California,
Berkeley, California, April 25, 1901.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxii., No. 18, May 6, 1901.

Osmotic Pressure across a Membrane of Copper Ferrocyanide.—G. Flusin.—An examination of osmotic pressure across those membranes said to be semi-permeable, like copper ferrocyanide, presents certain experimental difficulties. For the author's experiments, the membrane was precipitated on the internal side of a porous vessel, and solutions of the following substances were used:—A 2 per cent sugar solution, 1 per cent sugar solution, 1 per cent amygdaline solution, 1 per cent antipyrine solution, and a 1 per cent urea solution. The agreement between the numbers is very satisfactory, except for urea; and a study of these numbers shows that, for the same vessel, the velocities of osmose are proportional to the osmotic pressures, and consequently inversely proportional to the molecular weights.

Alloys of Aluminium. Combinations of Aluminium and Tungsten.—Léon Guillet.—The author makes a systematic study of certain aluminium alloys. He prepares the compounds by mixing the oxide of the metal whose alloy is desired with powdered aluminium, and, to excite the reaction of these two, he uses the medium of a powder of barium dioxide and aluminium. The first experiments were performed on tungstic acid, molybdic acid, magnetic oxide of iron, manganese oxide, tin binoxide, and titanic acid.

Mercury Iodoantimonide.—Albert Granger.—The author has already shown that mercury, when heated in presence of phosphorus iodide, is transformed into iodide and phosphide of mercury. He now finds that, in generalising this reaction, he can isolate arsenide, antimonide, and bismuthide of mercury. The present paper gives an account of the results obtained when mercury acts on antimony tri-iodide; a body is apparently obtained having a formula $Hg_5Sb_4I_4$.

A Specimen of Crystallised Lime.—Ad. Jouve.—Lime can be obtained in a prismatic form by suddenly cooling the mass of lime and carbon, just at the moment when the calcium carbide is on the point of forming. The carbon and lime to form the carbide are found respectively, the one in the form of graphite, the other of melted lime, sometimes even in the form of lime vapour. It is the cooling of this vapour in a closed space which probably produces the lime in prismatic crystals.

The Chemistry of Methylene.—V. Thomas.—The author's experiments on methylene show—(1) That mercury reacts on iodide of methylene (quite free from iodoform), with simultaneous formation of $CH_2I.HgI$, $CH_2(HgI)_2$, and $CH(HgI)_3$; (2) that the iodide, $CH_2I.HgI$, is decomposed under the action of heat, giving the derivatives $CH_2(HgI)_2$ and $CH(HgI)_3$; (3) that methylene iodide is decomposed by certain metals, with formation of ethane and methane (*e.g.*, mercury), or by others into acetylenic carbides, with precipitation of ammoniacal cuprous chloride (*e.g.*, silver).

Hydratation of Amylpropiolic Acid. Caproylacetic Acid.—Ch. Moureu and R. Delange.—The authors show—(1) That fuming sulphuric acid decomposes amylpropiolic acid with production of the fatty acid having at least two atoms of carbon; (2) that when the same acetylenic acid is treated with alcoholic potash, a non-substituted β-ketonic acid is obtained and caproylacetic acid. They propose to generalise these two reactions. The second constitutes a method of synthesis of the β-ketonic acids and ethers entirely different from the two other methods already known, of which one has been noticed by M. Bouveault and the other quite recently by M. Blaise.

Dimethylpyruvic Acid.—A. Wahl.—In a former paper, the author describes the preparation of dimethylpyruvic acid, $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH\!-\!CO\!-\!COOH$, a substance unknown up to the present time. He now endeavours to prepare dimethylpyruvamide by acting upon dimethylpyruvic ether with a concentrated solution of ammonia. An unexpected reaction, however, occurs, resulting in crystals possessing the composition $C_9H_{18}N_2O_2$. By further experiments, he succeeds in transforming dimethylpyruvic acid into α-isovalerianic oxide, and to fix in a certain and definite manner the constitution which was originally suggested for the above acid.

The Anhydride of the pretended Binaphthalene Glycol.—R. Fosse.—The author's experiments show that Rousseau's binaphthylene anhydride is identical with dinaphthoxanthene, $CH_2\!<\!\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}\!\!>\!O$. In a future research, the author hopes to establish the true nature of binaphthalene glycol.

Action of Acid Chlorides on the Ether Oxides in presence of Chloride of Zinc.—Marcel Descude.—When acetyl chloride and ethyl oxide in molecular proportion are heated together for some hours, no trace of reaction can be observed. The same thing occurs if any other ether oxide is taken, whether simple or mixed. If, however, a certain quantity of anhydrous zinc chloride is added, an immediate action takes place, with evolution of heat. The author investigates this reaction, using ordinary ether; it apparently takes place according to the following very simple equation:—

$$CH_3\!-\!COCl+C_2H_5\!-\!O\!-\!C_2H_5=$$
$$=CH_3\!-\!COOC_2H_5+C_2H_5Cl.$$

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxv., No. 2.

Research on Solutions.—G. Wyrouboff.—A very long paper, not suitable for abstraction.

On the Nitrocelluloses.—Leo Vignon.—Already noticed.

Reduction of Nitrocellulose.—Leo Vignon.—Already noticed.

Oxycelluloses from Cotton, Flax, Hemp, and Rush Pulp.—Leo Vignon.—Already noticed.

Cellulose, Mercerised Cellulose, Precipitated Cellulose, and Hydrocellulose. — Leo Vignon. — Already noticed.

Acetyl Derivatives of Cellulose and of Oxycellulose.—Leo Vignon and F. Gerin.—Already noticed.

Note on the Examination of Butter and Fats.—A. Reychler.—The author's attention having been directed to the examination of coco butter, which is a product relatively rich in insoluble volatile acids, he thought it would be of interest to determine, besides the Reichert characteristic, a figure which would be in relation to the total volatile acids. For this purpose he saponified 5 grms. of fat and followed all the succeeding operations of distillation, &c., in the usual manner, but, instead of filtering the distillate, he transferred it directly to a conical flask and placed a layer of 50 c.c. of alcohol over it. The floating droplets immediately disappeared, and on shaking the whole he obtained a slightly opalescent homogeneous liquor. The acidimetric titration was most simple, and gave a perfectly sharp and distinct terminal reaction. The results obtained by the two methods are set out in a table in two parallel columns, and in a third column the relation between the two is shown. This relation varies considerably, according to the nature of the fat under examination. With butter it reaches 0·90; that is to say, that on 100 molecules of volatile fatty acids, there are 90 soluble in water. With coco butter, the proportion goes down to 0·32. With oleomargarine and neutral lard, it takes an intermediate position.

MISCELLANEOUS.

The Estimation of Cerium.—G. von Knorre.—This method depends on the reduction of the yellow ceric salts to the state of colourless cerous salts, by means of peroxide of hydrogen in acid solution:—$2(SO_4)_2Ce + H_2O_2 = (SO_4)_3Ce_2 + SO_4H_2 + O_2$. The following is the method of working:—The solution is acidulated with the smallest possible quantity of dilute sulphuric acid, and persulphate of ammonium added in the cold; it is then boiled for one or two minutes, and cooled down to 40—60°, when a further quantity of persulphate is added, and the whole again raised to boiling for a few minutes; this cooling and the addition of persulphate is repeated a third time, after which the boiling is continued for ten to fifteen minutes. Finally, a slight excess of dilute sulphuric acid is added to decompose the persulphate. About 3 grms. of this salt are required for 0·2 or 0·3 grm. of cerium. The metal being thus completely peroxidised, titrated peroxide of hydrogen is added by means of a burette to the well-cooled solution, the point of decolouration being slightly exceeded. The excess of H_2O_2 is estimated by means of permanganate. The author compares his method with the similar ones devised by M. Job (*Comptes Rendus*, vol. cxxviii., p. 101), and W. Gibbs (*Zeit. Anal. Chem.*, vol. iii., p. 395), in which PbO_2 is used instead of persulphate.—*Berichte*, vol. xxxiii., p. 1924.

Examination of Commercial Nitrate of Thorium, and on the Incandescent Bodies in the Auer Burner.—W. Muthmann and E. Baur.—Starting from the fact that impurities considerably diminish the illuminating power of the incandescent substance in the Auer burner, the authors took some commercial nitrate of thorium, and, to its solution brought to boiling-point, they added drop by drop a solution of bichromate of potassium so as to effect a fractional precipitation. The first portions which came down consisted of a beautiful deep yellow microcrystalline precipitate of pure chromate of thorium, $(CrO_4)_2Th + 3H_2O$; it is only the very last portions which gave a dirty olive-green precipitate, or even no precipitate at all; they either no longer contained any thorium or only foreign oxides containing perhaps 0·3 per cent of nitrate of thorium. The thorium thus purified was incorporated with 0·01 per cent of peroxide of cerium, and then used for impregnating mantles. These turned out to be much more brilliant than the ordinary commercial ones, with a more yellow and less green light; their illuminating power was 1·3 to 1·4, taking as unity the "metathor" mantles made by Drossbach, of Freiberg. Thus we find that in the manufacture of mantles with well purified thorium, as the cerium is only present in very small quantities, its preparation does not require such great care.—*Berichte*, vol. xxxiii. p. 2028.

MEETINGS FOR THE WEEK.

MONDAY, June 3rd.—Society of Chemical Industry, 8. "The Need of Greater Care in Introducing Gas-firing into small Gas Works," by G. Cecil Jones. "The Chemical Aspects of Bacteriology," by Dr. Walter C. C. Pakes.

—— Royal Institution, 5. General Monthly Meeting.

TUESDAY, 4th.—Royal Institution, 3. "The True Functions of Poetry, and Wordsworth as a Teacher," by Churton Collins, M.A.

WEDNESDAY, 5th.—Society of Public Analysts, 8. "Arsenic in Coal and Coke," by Alfred C. Chapman, F.I.C. "Public Analysts' Records," by J. F. Liverseege, F.I.C. "The Composition of Milk and Milk Products" and "The Use of Partially Sterilised Milk Cultures in Judging the Purity of Water," by H. Droop Richmond, F.I.C.

THURSDAY, 6th.—Royal Institution, 3. "The Chemistry of Carbon," by Prof. Dewar, F.R.S., &c.

—— Chemical, 8. "A Laboratory Method for the Preparation of Ethylene," by G. S. Newth. "Oroxylin," by W. A. H. Naylor and G. S. Dyer. "Some Relations between Physical Constants and Constitution in Benzenoid Amines" (II.), by P. Gordon and L. Limpach. "The Constitution of the Acids obtained from α-Dibromocamphor," by A. Lapworth and W. H. Lenton. "The Decomposition of Chlorates—IV., The Supposed Mechanical Facilitation of the Decomposition of Potassium Chlorate," by W. H. Sodeau. "Condensation of Phenols with Esters of the Acetylene Series—V., Homologues of Benzo-γ-pyrone," by S. Ruhemann. "On the Action of Sodium Methoxide and its Homologues on Benzophenone Chloride and Benzal Chloride," by J. E. Mackenzie. "Preliminary Note on Hydrides of Boron," by W. Ramsay and H. S. Hatfield. "Gum Tragacanth," by C. O'Sullivan.

FRIDAY, 7th.—Royal Institution, 9. "Mimetic Insects," by Raphael Meldola, F.R.S.

SATURDAY, 8th.—Royal Institution, 3. "The Biological Characters of Epiphytic Plants," by Prof. J. B. Farmer, M.A., F.R.S.

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THE CHEMICAL NEWS.

Vol. LXXXIII., No. 2167.

ON THE

CIRCULATION OF SALT AND ITS BEARING ON CHEMICO-GEOLOGICAL PROBLEMS, MORE PARTICULARLY THAT OF THE GEOLOGICAL AGE OF THE EARTH.*

By WILLIAM ACKROYD, F.I.C., Public Analyst for Halifax.

Introduction.

Common salt, or sodium chloride, is probably the most widely distributed of all sodium compounds, as it is one of the most soluble. During our investigation of the underground waters of North-West Yorkshire, a fruitful aspect of its solubility was presented to us in the disappearance of 3 tons of salt in a runnel of 19,800 gallons per day; it went down the Smelt Mill Water Sink and reappeared after ten days at Malham Cove, where the amount of combined chlorine in the water suddenly rose from 1 up to 6 parts per 100,000, and in the course of another eight days slowly fell to the normal unit (*Proc. Yorkshire Geol. and Poly. Soc.*, vol. xiv., Part 1., p. 17). We had a similar experience at Clapham. It is apparent, therefore, that any salt in the soil or in underground channels is carried quickly away by the water; and such soil or underground channels would be thenceforth free from the compound unless in the course of disintegration fresh quantities were exposed for solution. This, however, is so slow a process that it quite fails to account for the enormous amounts of chloride annually conveyed by rivers to the sea.

The position is perhaps better seen in the following statement of fact:—The Widdop reservoir, belonging to the Halifax Corporation, contains some 640·5 millions of gallons of water, and I estimate it to contain 55 tons of salt. The two thousand odd acres of gathering ground is moorland on millstone grit for the most part with a little of the Yoredale rocks. Needless to say, it is a saltless area; yet the 55 tons of salt is renewed probably more than once a year in the course of filling up to replace the Corporate demands on the reservoir. The chlorides come down in the rain-water. We may take it, then, as a working hypothesis, that rain has brought down the salt, which has been derived from the sea, and that to the sea it quickly returns. It will be convenient to speak of this salt as *sea-salt*, in contradistinction to such as may be derived from the earth by solvent denudation, which will be referred to as *earth-salt*, and the proportionate amount of the sodium compound will be indicated in this paper by the chlorine figure.

Circulation of Sea-salt.

The conditions obtaining in the Widdop area are of more than ordinary scientific interest, and I have made an experimental investigation of them during the winter 1900—01, which has been communicated to the Chemical Society of London (*Trans. Chem. Soc.*, lxxix., p. 673). It will suffice to recount here that from November 12 to February 18 weekly chlorine determinations were made of the reservoir water, of the water in a rain-gauge kept close by, and of rain-gauge water on four other gathering-grounds some miles to the east of Widdop—viz., Walshaw Dean, Midgley, Warley, and Ovenden Moors,—besides daily tests of rain-gauge water from Belle Vue in the town of Halifax.

The reservoir water was fairly constant with an average of 1·188 parts of chlorine per 100,000. This figure will be greater than that of the annual average rainfall, on account of evaporation, and if we deduct 10 per cent, it would still be equivalent to a fall of 172 lbs. of common salt per acre with the 1899 rainfall of 43·17 inches.

The rain-gauge figures fluctuated wildly; Widdop rain-gauge water reached 3·3 per 100,000 during a December week when a violent storm was blowing from the Irish Sea about 40 miles away, and on another occasion it got up to 6·5; the average for the fourteen weeks of observation was 1·53. That the winter average should be in excess of the yearly average is in keeping with the results obtained by other observers, and gives some idea of the activity of salt circulation during the stormy part of the year when gales are prevalent from the sea. The abnormally high figures obtained at Widdop synchronised with similarly high figures for the other gathering-grounds.

Observations on chlorine in rain-water have been made at Cirencester since 1870 by Professors Church, Prevost, and Kinch (*Trans. Chem. Soc.*, vol. lxxvii., p. 1271). An abnormal amount of chlorine has almost always been traced by them to salt spray from the Bristol Channel 35 miles away. On different occasions, immediately after a storm from the S.W., crystals of common salt have been found on the College windows facing west. The same kind of evidence has been furnished to me by Mr. J. H. Howarth respecting Malham, concerning Leeds by Mr. J. E. Bedford, and Mr. J. Denison calls my attention to the following references:—"The winds from the south-west have sometimes blown so strong that the pieces of cloth on the tenters in several parts of Halifax parish have been charged with a considerable number of saline particles brought from the sea" ("Watson's History of Halifax," 1775, p. 5); and, further,—"Sea-salts have been found deposited on the windows in West Park and York Place (Harrogate), thus giving practical evidence of the presence of the sea-breeze" ("The Use and Abuse of Harrogate Mineral Waters," by Arthur Roberts, p. 32).

Table I. is a synopsis of results up to date, the chlorides in the rainfall being calculated into annual downfall of salt per unit area.

As to the particular nature of this salt circulation, we may suppose—(1) That salt spray from the sea is carried to the land to distances varying with the force of the wind; (2) that when the salt is dried by evaporation it is carried further inland with the dust; and (3) that rains dissolve it and bring it down to the rivers by which it is carried back to the sea.

Of the carrying of the salt spray abundant evidence, as I have shown, has been obtained in times of storm, and of the presence of sodium in dust at all times the spectroscope yields never-failing proof, while in the examination of rain-water I have found the highest chlorine contents in light rain-falls.

The full extent inland of salt circulation has yet to be determined; it may not be entirely limited by mountain chains barring the direction of prevalent sea-winds, as finely divided sea-spray may possibly be carried nearly as far as the dust of Krakatoa. This much, however, we know, that the further one gets inland, the less the chlorine figure becomes for rain-water. Angus Smith has published some averages for rain ("Air and Rain," Longmans, London, 1872, p. 281), in terms of hydrochloric acid per million. The following are his figures converted to chlorine in parts per 100,000 of rain-water:—

Ireland, Valentia	4·72
Liverpool	3·49
English towns	0·84
Darmstadt	0·094

The Concentration of Sea-salt.

When rain-water reaches the earth its burden of salt necessarily becomes concentrated by evaporation. A sheet of water will in twelve months lower its level 20

* Read before the Yorkshire Geological and Polytechnic Society, at Leeds, April 25, 1901.

Table I.

	Distance from the sea. Miles.	Deposit of NaCl per acre per year.	Observers.
Cirencester	35	36 lbs. (average of twenty-six years)	Church, Prevost, and Kinch (*Trans. Chem. Soc.*, vol. lxxvii., p. 1773).
Rothamsted	—	24·59 lbs. (average of six years)	Lawes, Gilbert, and Warington (*Ibid.*).
Perugia	75	37·8 lbs.	Bellucci (*Ibid.*).
George Town, Demerara	—	186 lbs.	Harrison (*Ibid.*).
Widdop	40	172 lbs.	Ackroyd.

Table II.

	Parts per 100,000.		Ratio.		
	Total solids.	Cl.	Total solids	:	Cl.
Upland surface water (average of 19 analyses, extending over two and a half years, Sept., 1898, to Jan., 1901).	9·68	1·33	100	:	13·7
Well No. 1 (pure)..	38	3·85	100	:	10·1
„ 2 „	28	2·00	100	:	7·1
„ 3 „	38	2·15	100	:	5·7

inches,* so that it follows if the original depth were 40 inches, the result of a year's evaporation would be to double the amount of salt in the residual water; much quicker must evaporation be from land surfaces, where capillary action may come into play, and consequently draw moisture upwards where it is exposed on a maximum of earth surface to the evaporative influence of the sun or of a higher atmospheric temperature.

The final result appears so apparent as to need no proof. I may, however, refer to peculiar cases of concentration I have come across in the course of this study. Well waters in the millstone grit show evidence of concentration in higher chlorine figures, and also that the salt is cyclic *sea-salt* from the fact that *it does not increase at the same rate as the other solids in solution*, whereas, it it were derived from the soil it ought to increase at a greater rate, because of its greater solubility than that of the other bodies. The data given in Table II. will illustrate the point.

The Caspian and Dead Seas.

This concentration of chlorides is an important geological factor. To return to our Pennine reservoir:—If there were no outlet, and a rate of evaporation equal to the inflow of water, it would, in 50,000 years, contain 2½ millions of tons of salt; or, if we halve the rate of accumulation, it would still be 1,375,000 tons of salt, collected from a gathering-ground of 2223 acres into a reservoir of 93 acres surface and of a depth of 65 feet. The water at this lesser estimate would contain 32 per cent of salt, as compared with the Dead Sea with its 24 per cent; and the accumulation, derived nearly entirely from rain-borne sea-salt, would have been amassed during a period which is comparatively trifling, as geological time is reckoned, being probably less than a seventh of the Pleistocene age.

We have here, then, a process at work which must be taken into account in framing theories of salt-lake and salt-deposit formations; hitherto it has been entirely overlooked, and only contributions of earth-salt derived by solvent denudation have been drawn upon for the purpose, with in many cases the added supposition that the first step in their formation was the disconnection of an arm of the sea—a supposition which is not always required. Thus, with regard to the salt deposits of Northern Africa, Prof. Zittel (*Nature*, vol. xxix., pp. 121 and 122) has shown, on what appears to be overwhelming evidence, that the popular idea of the Sahara having been the basin of a sea in Pleistocene times is without foundation, and —as the rainfall was heavier and the climate damper in those days than now—rain-borne sea-salt must have played an important part in the formation of the salt hills of the Sahara.

The usual theory of the cause of the saltness of the Caspian Sea appears also somewhat anomalous. The Mediterranean, Black Sea, Sea of Azof, and Caspian Sea decrease in saltness in this order, on which Ramsay (*Nature*, vol. vii., p. 313) has remarked:—"It will be seen that the Black Sea is fresher than the Mediterranean. The Caspian is still fresher, and its fauna and fossils in recent deposits in the neighbourhood prove it to have once had connection with the Black Sea, from which it has been separated by changes in physical geography; it was then salter than at present, but is now growing salter again every year, and the fauna now inhabiting its waters have likewise considerable affinities with North Sea types." Now I should think the whole physical facts of the case are comprised in the simple statements that the Caspian is an inland sea, of large volume and variable composition, fed by inland rivers rising in and flowing through regions where the sea-salt in the rainfall—not reckoning that derived from the lake itself—must have reached a minimum, where the chief source of the saltness must be the earth-salt from solvent denudation, and how small that may be expected to be will be presently shown in the case of the Aire at Malham Cove, where a large portion of the evaporated water must come down again to the sea itself, so large is its area; from all of which statements it follows that the Caspian must increase in saltness at so phenomenally slow a rate that one is not surprised to find it least salt of all the waters which have been mentioned. As an inland lake, without outlet, one would think that it can never have been salter than it is at present, and it will be well to revise the biological data upon which such an idea is based.

Let us next consider the Dead Sea from this point of view. Little further removed from the Mediterranean than Widdop is from the Irish sea, with a rain-fall in Palestine higher than that of the Pennine hills, and an intensity of meteorological conditions in the past of which we can at the present day form but a poor conception (Tristram, "The Land of Israel," p. 320), it is reasonable to suppose that the salts in the Dead Sea have been for the most part derived from the Mediterranean, carried by winds and brought down by rains, and barring the contributions of Jebel Usdum it will probably be found that over 90 per cent of the salts come from this source. On such a theory we look for some measure of likeness between the dissolved matters of the two waters, but an initial obstacle to comparison presents itself in the much greater concentration in one case than in the other, and in the variability of the Dead Sea itself from the north where the Jordan enters to the south, where the salt hill

* A four years' mean annual evaporation from the Torquay watershed, as kindly supplied to me by Mr. W. Ingham, C.E., is 20·88 inches, 1897—1900.

of Jebel Usdum overlooks it. In instituting a comparison I have therefore confined myself to the ratio of the related ions chlorine and bromine. Usiglio's figures for the Mediterranean at Cette give :—

Cl.		Br.
100	:	2·1

which are practically the same as Von-Bibra's for the Atlantic at the Equator :—

Cl.		Br.
100	:	2·09

The analyses of Dead Sea surface water made by Terreil give the following ratios :—

	Cl.		Br.
Near Rasdale	100	:	0·95
Lagune North of Sodom ..	100	:	2·7
Near island	100	:	3·6
Average	100	:	2·4

The closeness of this average to the Mediterranean and Atlantic Ocean figures is somewhat remarkable, and although it will not be taken as absolute proof that the Dead Sea has derived its salt from the Mediterranean, it at least destroys the contention that the dissolved constituents of the two seas are so dissimilar that one cannot have been derived from the other.

The Geological Age of the Earth as measured by the Rate of Solvent Denudation.

I now pass to the bearing of the foregoing facts, and others I shall adduce on Prof. Joly's way of deducing the age of the earth since the first ocean was formed. The method may be thus briefly put :—

$$\frac{NaCl + NaNO_3 + Na_2SO_4 \text{ in the seas}}{\text{Annual addition of } NaCl + NaNO_3 + Na_2SO_4 \text{ by rivers}} = \text{Age of the earth,}$$

or more particularly the sodium contents of the seas divided by the sum of the annual sodium increments furnished by the affluent rivers equals the geological age of the earth.

There can be no mathematical precision in any method for getting at the age of the earth, and notwithstanding the marked circumspection shown by Prof. Joly in dealing with the facts available to him, this latest method of attacking the problem appears no more precise than the rest.

If we take the numerator to be approximately correct, the degree of accuracy attainable will depend upon the reliability of the denominator, and to this question my attention will be solely directed.

It is assumed in the first place that the solvent denudation which yields the annual load of combined sodium to the seas has been uniform in its action from the first. Now as a chemist I have tried to picture to myself the condition of things immediately before and after the "consistentior status," when the cooling globe allowed of the condensation of aqueous vapour to form the first ocean.

Oxides of the alkalis and alkaline earths, silicated and otherwise, would exist among the first compounds; hydrochloric acid would admittedly be another, and as the temperature gradually lowered their incompatibility would result in the production of silica, aqueous vapour, and salts like sodium chloride.

There is no more remarkable fact than the thoroughness with which hot water takes up chlorides from a hot surface with which it is in contact or prevents their deposition. I need only instance the formation of boiler scale. The boiler water increases the amount of its chlorides in solution so regularly with the amount of evaporation that it has been made the basis of a technical method, now often used, for finding the evaporative power of coal; the boiler scale contains only the minutest trace of chlorides.

I imagine, then, that the seething Archæan Sea would dissolve all soluble chlorides from the ocean floor and rocks of those times; and as the deliquescent salts appeared on new land surface they would be washed away by every shower, so that to all intents and purposes "the sea was salt from the first." My ideas here run somewhat parallel to those of Prof. W. J. Sollas, who in his able address to the Geological Section of the British Association at Bradford, observes :—"The ocean when first formed would consist of highly heated water, and this, as is well known, is an energetic chemical reagent when brought into contact with silicates like those which formed the primitive crust. As a result of its action saline solutions and chemical deposits would be formed; the latter, however, would probably be of no great thickness, for the time occupied by the ocean in cooling to a temperature not far removed from the present would probably be included within a few hundreds of years" (*B. A. Report*, 1900, p. 716).

This view of things is opposed to uniformity of rate of solvent denudation, and leads to the direct inference that in the later age of the earth such changes are proceeding at a very much slower rate. I see no objection to a varying rate in the facts adduced by Dr. Joly as confirmation of his hypothesis of uniformity from the first. He points out that the sum of the soda now in the ocean and in the sedimentaries would nearly suffice to effect the full restoration of this constituent to the original igneous rock. Such facts are equally in keeping with an unequal distribution of the work of denudation over the period of the earth's age, that it was rapid at first and afterwards slower and slower with the flow of time, and the slower the rate at which one can prove it to be now proceeding, and the more prodigious must have been the initial rate to yield the final colossal sum of oceanic contents.

On the Ratio of Sea-salt to Earth-salt in River-Water.

It will be apparent that if we have to get an idea of the rate at which solvent denudation is now proceeding it will be necessary to find what proportion of earth-salt rivers are carrying to the sea along with the cyclic sea-salt. I have to offer the following attempt at a solution of the problem for the source of the Aire.

A gravimetric analysis of Craven limestone gave 0·01 per cent of chlorine. The water at Malham Cove is 10° of hardness, and contains a total 0·7 part of chlorine per gallon. It is included in that area of equal chlorine figures (Ackroyd, *British Association Report*, 1900, p. 695) where at least in one case, that of Widdop, I have proved all the combined chlorine comes from the rain. Therefore every gallon of water at the Cove contains :—

	Grains.
Calcium carbonate	10·000
Chlorine in earth-salt	0·001
Chlorine in sea-salt	0·699

or of the load of salt carried to the sea fully 99·8 per cent is sea-salt, and only less than 0·2 per cent earth-salt, or that part which is to be taken into account in ascertaining the rate of solvent denudation now in progress, and even this is cyclic in a sense as it comes from a carboniferous and goes back to a present day sea.

How does this result square with other facts? Lawes, Gilbert, and Warington (*Trans. Chem. Soc.*, vol. li., p. 94), have shown that the amount of chlorides in drainage from drain-gauges in unmanured land and uncropped soil is almost exactly equal to that contained in the rain. In other words, they were unable to estimate the amount of earth-salt, it was so small. Again, in chalk, granite, sandstone, and other rocks, the sodium chloride is so inconsiderable a trifle as to find no place in recorded analyses. It is improbable, then, that after extended investigations, an average of 1 per cent of the sodium carried to the sea as chlorides, &c., will ever be found as the result of solvent denudation, and consequently that Prof. Joly's 90 millions of years estimate of the age of the earth based on uniformity of action, and a deduction of 10 per cent for cyclic

sea-salt, would become 8000 millions of years, a quantity of time which I imagine will be too excessive even for the exorbitant demands of the biologists.

Seasonal Variation of Salt Circulation.

In all such problems again seasonal variation of fluviatile salt load must also be taken into account. It has a tendency to average itself where large volumes of water are concerned; thus, in the hundreds of samples analysed from the source of the Aire during our investigations of the underground waters, there has been no noticeable variation from normal; these, however, have only been summer experiments. There must be variations due to periods of excessive evaporation and of storm. The summation of such effects is shown strikingly in the case of the Nile. Wanklyn ("Water Analysis," Sixth Edition, p. 151), in 1874 and 1875 obtained the following chlorine figures for this river:—

	Parts per 100,000.
1874, June 8	2·5
July 9	1·3
August 12	0·4
September 20..	0·5
October 12	0·5
November 12	0·7
December 12	0·6
1875, April	1·4
May 13	1·7

Similar observations are wanted for all the rivers of the world.

Conclusion.

To sum up, then, salt circulation in nature forms an important and up to now inadequately realised phenomenon. In the solvent denudation method of arriving at the age of the earth too little allowance has been made for the mass of sodium chloride carried by the rivers which has been derived from the ocean by atmospheric transportation, and consequently too high a figure (viz., 5·73 parts per million, which is the equivalent of 0·88 part of chlorine per 100,000), has been adopted for the variable proportion of sodium derived from the earth. But although little satisfaction may be derived from numerical results obtained by this in common with other methods, they are at least welcome in that we are led to garner and make use of an abundance of facts which lie to hand and only need the trouble of reaping.

SATURATED LIME-WATER FOR THE PRESERVATION OF EGGS.

By FRANK T. SHUTT, M.A.,
Chemist, Dominion Experimental Farms.

THE solubility of lime in water at ordinary temperatures is 1 part in 700 parts of water. Such a solution would be termed saturated lime-water. Translated into pounds and gallons this means 1 lb. of lime is sufficient to saturate 70 gallons of water. However, owing to impurities in commercial lime, it is well to use more than is called for in this statement. It may not, however, be necessary if good, freshly burnt quicklime can be obtained, to employ as much as was at first recommended, namely, 2 to 3 lbs. to 5 gallons of water. With such lime as is here referred to one could rest assured that 1 lb. to 5 gallons (50 lbs.) would be ample, and that the resulting lime-water would be thoroughly saturated. The method of preparation is simply to slake the lime with a small quantity of water, and then stir the milk of lime so formed into the 5 gallons of water. After the mixture has been kept well stirred for a few hours it is allowed to settle. The supernatant liquid, which is now "saturated" lime-water, is drawn off, and poured over the eggs previously placed in a crock or water-tight barrel.

As exposure to the air tends to precipitate the lime (as carbonate), and thus to weaken the solution, the vessel containing the eggs should be kept covered. The air may be excluded by a covering of sweet oil, or by sacking upon which a paste of lime is spread. If after a time there is any noticeable precipitation of the lime the lime-water should be drawn or syphoned off and replaced with a further quantity newly prepared.

It is essential that attention be paid to the following points:—

1. That perfectly fresh eggs only be used.

2. That the eggs should throughout the whole period of preservation be completely immersed.

Although not necessary to the preservation of the eggs in a sound condition, a temperature of 40° to 45° F. will no doubt materially assist towards retaining good flavour, or rather in arresting that "stale" flavour so characteristic of packed eggs.

Respecting the addition of salt, it must be stated that our experiments—conducted now throughout three seasons—do not show any benefit to be derived therefrom; indeed, salt appears to impart a limey flavour to the egg, probably by inducing an interchange of the fluids within and without the egg.

Water-glass (sodium silicate), has been extensively experimented with, using solutions varying from 2 to 10 per cent. Although in the main the results have been fairly satisfactory, we are of the opinion that lime-water is fully its equal, if not its superior, as a preservative, and that this latter preservative is both cheaper and pleasanter to use there can be no doubt.

ON THE USE OF PERMANGANATE OF POTASH IN DYEING.

By G. SAGET.

PERMANGANATE of potash can be used in dyeing for obtaining light bistre or tawny tints. Its oxidising action is utilised for destroying any given background by the production of peroxide of manganese in the body of the fibre.

The backgrounds obtained with a tannin material and a metallic salt are very easily destroyed, and the bistre tint is obtained with great facility.

Tannins generally have a very good action on cotton fabrics, the final tint obtained being very regular; this latter varies according to the quantity of tannin used, and therefore an excess of permanganate need not be feared.

The reduction of the permanganate takes place very rapidly in the cold; any increase of temperature must be avoided or the permanganate will be reduced by the cellulose, and the tint will not be uniform, as it varies with the temperature.

Chestnut-brown and iron are particularly useful in obtaining unbleached tints. If, for example, we apply extract of chestnut, then pyrolignite of iron, and, after a sufficient time wash, and pass the material through a cold dilute solution of permanganate of potash, at the end of a quarter of an hour the brown colour will have entirely disappeared and given place to an unbleached tint, which will be the deeper as the original brown was the more intense.

Extract of yellow wood, cachou, &c., may be used instead of extract of chestnut, but the tints obtained will be practically the same.

Other metallic fixers of tannin may be used instead of iron; with antimony we obtain a less reddish tint than with iron. In the case of this latter, ferric oxide is formed, which adds its colour to that of the peroxide of manganese.

The tannates of lead, copper, chromium, alumina, manganese, &c., give the same results.

The salts of manganese and lead give deeper shades than those of the other metals. This is due to the fact

that peroxides of manganese and lead are formed, the deep colours of which are added to that of the manganic oxide resulting from the reduction of the permanganate.

The colourless, or slightly coloured oxides, like those of antimony, alumina, and chromium, give the palest tints; this, of course it must be understood, is when using the same quantities of tannin and permanganate, and equivalent amounts of the metallic salts.

The metallic salts which give the best results are those which most effectually fix the tannin, and among these are the acetates.

Putty-colour tints, obtained by the oxidation of the tannins by means of the bichromates alone or with the addition of salts of copper, also reduce permanganate; in this manner we obtain a light brown colour, appearing yellowish by reflected light.

Plumbite of lime fixed on the fibre also reduces permanganate of potash, a maroon colour looking red by reflected light is obtained; this is formed by a mixture of peroxides of lead and manganese.

The tints obtained as above strongly resist the action of hypochlorites. When immersed in "javelle" water the tint does not change. Boiling soap degrades and tarnishes the colour.

Sunlight has a very rapid action on these colours; after two hours' exposure to the summer sun the tint becomes decidedly paler; treatment with chlorine will revive it. Oxycellulose is not formed by this reduction in the sun. It is nevertheless possible to give greater permanence under the action of light to tints obtained as above described.

Treatment in a soda-salt at 60° for half an hour does not change the shade, but it will then resist the action of sunlight very well. When boiled, the soda-salt fades the tint to a slight extent, without making it any more permanent than when treated at 60°. The same can be said with regard to treatment in the cold by hypochlorite of lime at ½° Baumé, followed by thorough rinsing.

Ferric nitrate also gives greater permanence, under the action of light, to tints obtained with manganese, but the shade becomes a little more yellow. This last treatment also enables the colour to resist the action of soap better. Steaming, with or without pressure, degrades the tint considerably, and it cannot then be revived by chlorine.

Acids, even when dilute, soon cause the colour to disappear; when placed in citric acid at 1 per cent a sample became quite white in half an hour.

Bisulphite of soda instantly bleaches bistre, leaving the tissue perfectly white. The same is the case with mineral and organic reducing agents.

When applied to oiled tissues these neutral tints are much more permanent, especially if care be taken to treat them with soap at 60° after the washings which follow the treatment with permanganate of potash. Their resistance to light is good, and steaming, which has no effect on the colour, gives it more stability with acids.

Tissues may be prepared with oil for a reddish colour, or the oil may be added to the tannin material made alkaline with ammonia. In this case the pieces must be dried before passing them through the metallic bath.

With oil, the shade is greyer than with ordinary tissues, and approaches the colour of otter fur. Soap still slightly degrades the colour, but when once soaped and steamed without pressure, its resistance may be looked upon as sufficient.

Alumina increases the resistance of tints formed by tannate of iron oxidised by permanganate of potash to dilute acids; and in the same way a shade obtained with manganese and acetate of alumina, and then dried and steamed without pressure, hardly changes at all in a solution of 1 per cent citric acid. Its resistance to soap is fairly good, but in sunlight it fades rapidly.

The drying with an aluminium salt produces a yellowish tone, which disappears again on steaming.

On the other hand, the tint produced by fixing the tannin with an aluminium salt, and then, after oxidation in permanganate, treating with acetate of iron, drying, and steaming without pressure, does not resist the action of soap, hypochlorites, dilute acids, or light. It is just the same if, instead of using an aluminium salt for fixing the tannin, we use a salt of antimony.

Binoxide of manganese fixed on the tissue, as we have shown above, may serve as a mordant for various colouring materials, and at the same time as an oxidising agent for certain aromatic amines.—*Moniteur Scientifique*, Series 4, vol. xv., p. 319.

THE LITERATURE OF ALCHEMY.*

By HENRY CARRINGTON BOLTON.

(Continued from p. 262).

The Greek manuscripts of the eleventh to the fourteenth centuries, collected, translated, and edited by Berthelot, vary in length from fragments of a few lines to essays of many pages; all are written in an archaic, enigmatical style puzzling to decipher; names of mythical personages, chemical expressions of obscure meaning, magical formulas, astrological computations, are mixed in singular confusion with allusions to a long forgotten, mystical philosophy. Commentators on these writings of the "Sacred art" early felt the need of lexicons and compiled vocabularies professing to throw light on them, but their definitions are no clearer than the words defined; one word was used for a score of different articles, and a single object or process was known by a dozen different names. Of scientifically classified knowledge there is no trace, the alleged opinions of fabulous writers are given as authoritative, and information is imparted in the tedious form of dialogues. Many of the writings contain reverent acknowledgment of the Deity and other evidences of piety.

The titles of a few of these MSS. will give an idea of the nature of the literature at this period.

"The Chemistry of Moses."
"Letter of Isis to her son Horus."
"Cleopatra on the art of making Gold."
"The divine Zosimus on Virtue."
"Zosimus on Furnaces and Apparatus."
"The Whitening of Arsenic."
"The Practical Treatise of the Emperor Justinian."

The authors of these essays are unknown, and they are practically a farrago of nonsense.

The most ancient Latin treatises on alchemy date from the eighth to the tenth century; they are really collections of recipes for industrial processes and metallurgical operations, but include formulas for the manufacture of gold, and for "multiplying" the precious metal, resembling those of the Greco-Egyptian papyri. The readers are cautioned not to reveal the secrets and are instructed in the use of appropriate incantations. The manuscripts of these Latin writings are seldom met with, but they were printed in several great collections published in the seventeenth and eighteenth centuries; the most notable of these were the "Aureum Vellus" (Basel, 1599); "Artis Auriferæ" (Basel, 1572), containing 34 treatises; "Theatrum Chemicum," published by Lazarus Zetzner (Strassburg, 1613—22, 5 vols.; second edition, 1659—61, 6 vols., containing 149 titles); "Bibliotheca Chemica Curiosa," edited by J. J. Manget (Geneva, 1702), containing 133 titles.

More than half a century elapsed after the invention of printing before the subject of alchemy occupied the press, but in the sixteenth and seventeenth centuries thousands of works printed in every country of Europe supplied the universal demand for a literature that revealed secrets enriching and exalting its fortunate possessors. The most highly revered treatises were those ascribed to mythical Egyptians, to Old Testament Hebrews, to Arabian physicians, and to Greek philosophers; and at a later period the most popular works were those written by certain dignitaries of the Church. The genuineness of the trea-

* From the *Pharmaceutical Review*, vol. xix., Nos. 4 and 5.

tises was not questioned, and the fact that their teachings were contrary to reason did not diminish their popularity.

In the sixteenth century the favourite authors were Roger Bacon, an English Franciscan, Albertus Magnus, a German Dominican, Raymond Lully, a Spanish Minorite, and Basil Valentine, a German Benedictine; somewhat later the hermetical writings of that bombastic Swiss physician Paracelsus were much in demand, and following him there came a host of lesser lights whose names are quite unknown outside of this contracted field.

A prominent feature in alchemical literature is the bold claim of fabulous antiquity for the art; this has been referred to in speaking of fictitious authorship, and may well be illustrated by citing the famous "Tabula Smaragdina"; its story runs thus:—

Hermes Trismegistus, who is identified with Canaan, the grandson of Noah, was perfectly acquainted with the Philosophers' Stone, and wishing to transmit the knowledge to posterity had the secret of its preparation engraved on a tablet made of a huge emerald, and had it placed in his sarcophagus. Many years afterwards it was removed by Sarah, the wife of Abraham, and concealed in a cave near Hebron; there it remained until again discovered by Alexander the Great. The inscription reads as follows:—

"I speak not fictitious things but that which is most true and certain. Whatsoever is below is like that which is above, and that which is above is like that which is below, to accomplish the miracles of one thing. Also since all things were made from one by the help of one, so all things are made from one thing by conjunction.

"The Father thereof is the sun, and the Mother thereof is the moon; the wind carries it in its belly, and the nurse thereof is the earth. This is the foundation of all wisdom, and its power is perfect if it be changed into earth.

. . . . .

"This thing has more fortitude than fortitude itself; because it will overcome every subtile thing and penetrate every solid thing. By it this world was formed. Hence proceed wonderful things which in this wise were established.

"For this reason I am called HERMES TRISMEGISTUS, because I possess three parts of the philosophy of the whole world.

"What I had to say about the work of the sun is completed."

The first appearance of this phantasy is not certain; some claim it is found in a work by Albertus Magnus, others trace it back to Hortulanus in the eleventh century; it was certainly known to Raymond Lully.

Pretentions to even greater antiquity were made by the anonymous author of "Gloria Mundi," in which we find the chemical notions of Aristotle, Plato, and Socrates, interspersed with statements by Hermes and Morien, Lamech and Methuselah, Abel and Seth, and even of Adam himself.

(To be continued).

The presence of Saccharose in Panama Wood.—G. Meilliere.—The presence of a hydrate of carbon has been observed several times in Panama wood (*Quillaja smegmadernos*). Up to the present it has been thought that this sugar was identical with the lactosine isolated from various caryophylls by A. Meyer. When the sugar from Panama wood is purified by means of a large number of crystallisations and by dialysis, it loses the property of frothing which was evidently due to the presence of a small quantity of saponine. The carbohydrate thus prepared has all the physical and chemical properties of saccharose. Without wishing to deny the possible existence of Meyer's lactosine in certain saponine plants, the author is of the opinion that the lactosine from Panama wood is nothing else but saccharose contaminated with saponine.—*Bull. Soc. Chim.*, Series 3, vol. xxv., No. 2.

ON THE RESULTS OF A SEARCH FOR OTHER SUGARS THAN XYLOSE AND DEXTROSE IN THE PRODUCTS OF THE HYDROLYSIS OF WOOD FROM THE TRUNKS OF TREES.*

By F. H. STORER, Professor of Agricultural Chemistry.

(Continued from p. 258).

C. *Acid Hydrolysis of Wood from the Trunk of a Birch Tree* (*Betula populifolia of Aiton*).—The wood submitted to examination was the outer part of the trunk of a grey birch tree four inches in diameter that had been felled in the month of October. After the outer and inner bark had been removed, that portion of the outer wood which lay between the bark and a circle drawn half an inch inward from the bark was split off, and ground to a fine powder. Ten grms. of this powder were soaked in 200 c.c. of strong ammonia water for twenty-four hours to remove colouring matters and albumenoids, and the excess of ammonia was removed by washing. The wood was then mixed with 200 c.c. of hydrochloric acid of 3 per cent, and boiled for three hours, over a free flame, in a flask provided with a reflux condenser. One half of the filtrate from the wood thus treated was neutralised with sodium hydroxide, evaporated, decolorised with bone-black, and tested. It gave quasi-$[\alpha]_D = 62{\cdot}85°$ and 19·8 per cent of "sugar," calculated as dextrose on the wood dried at 100° C.

On evaporating the solution to dryness, and treating the dry mass with cold, strong alcohol, there was obtained a residue which gave quasi-$[\alpha]_D = 76{\cdot}81°$, while the portion soluble in alcohol gave quasi-$[\alpha]_D = 24{\cdot}52°$; both observations being made, of course, upon aqueous solutions after the alcohol had been driven off—the references are to dextrose. It is evident that the matter insoluble in alcohol contains some substance of higher rotatory power than dextrose, while as regards the portion soluble in alcohol it is to be inferred that it contained much xylose, the true specific rotation of which is $[\alpha]_D = 19{\cdot}2°$. Calculated as dextrose, the matter insoluble in alcohol amounted to 4·65 per cent of the dry birch wood, and the sugar soluble in alcohol to 12·54 per cent.

The second half of the filtrate, from the three hours' boiling with hydrochloric acid of 3 per cent, was now boiled three hours longer, and neutralised and decolorised as before. It gave quasi-$[\alpha]_D = 40{\cdot}54°$, and "dextrose" amounting to 9·97 per cent of the dry wood, showing that in the absence of wood some of the products of the first hydrolysis were readily destroyed by the hot dilute acid.

On evaporating this solution to dryness and treating the residue with cold, strong alcohol, the matter less soluble in alcohol gave quasi-$[\alpha]_D = 42{\cdot}27°$, and the readily soluble portion gave quasi-$[\alpha]_D = 22{\cdot}17°$.

The residual cellulose from the wood which had been boiled with 3 per cent hydrochloric acid was washed and allowed to dry in the air; it was then left to soak for twenty-four hours in 100 c.c. of hydrochloric acid of 35 per cent, and the mixture was poured into enough boiling water to reduce the acid to the strength of 3 per cent. The mixture was boiled during three hours over a free flame, as before. Evidently the strong hydrochloric acid had but little action upon the wood.

One half of the filtrate was neutralised with sodium hydroxide, evaporated, and decolorised. It gave quasi-$[\alpha]_D = 85{\cdot}7°$, and dextrose equal to 0·98 per cent of the dry residue, or to 0·78 per cent of the dry wood. It is to be remarked, however, that this observation is of little or no value, because the solution was extremely dilute. It contained absolutely too little sugar to admit of a satisfactory examination. Nevertheless, it was evaporated to dryness, and treated with cold, strong alcohol. The portion soluble in alcohol gave quasi-$[\alpha]_D = 53{\cdot}34°$.

* *Bulletin of the Bussey Institution*, 1900, vol. ii., Part 9.

The second half of the filtrate, obtained after soaking in strong hydrochloric acid, and subsequently boiling in this acid diluted to 3 per cent, was boiled three hours longer, but so little sugar was contained in the liquid that no tests could be made. It is noticeable that hydrochloric acid of 35 per cent has no such power to break up the cellulose in wood as is exhibited constantly by strong sulphuric acid.

The residual wood left after the treatment with strong hydrochloric acid, and subsequent boiling with the 3 per cent acid, was mixed thoroughly with 10 c.c. of strong sulphuric acid (90 per cent H_2SO_4), and left at rest for twenty-four hours. The black, pasty mass was poured into enough boiling water to reduce the strength of the acid to 3·5 per cent, and the mixture was boiled for three hours. The filtered solution was neutralised with calcium carbonate and tested. It did not need to be decolorised. It gave quasi-$[\alpha]_D = 92°9'$, and 23·72 per cent of sugar, calculated as dextrose on the dry residue—or 18·83 per cent calculated on the dry wood. When this solution was evaporated and treated with cold, strong alcohol, the matter left undissolved gave quasi-$[\alpha]_D = 71°60'$, and the portion soluble in alcohol gave quasi-$[\alpha]_D = 54°93'$. On again evaporating the aqueous solution of the matter not dissolved by alcohol, and treating the new residue with cold, strong alcohol—in order to dissolve out as much dextrose as might be possible—there was obtained a new fraction insoluble in alcohol which, on being dissolved in water, gave quasi-$[\alpha]_D = 85°88'$. There was not enough matter dissolved by the alcohol to admit of any critical examination, but the solution was set aside to evaporate, and after six months it was noticed that the solid residue had segregated in the form of isolated tufts or balls (presumably of dextrose), rising from the centres of thin, star-like radiations of crystals.

The second half of the filtrate from the hydrolysis with sulphuric acid of 3 per cent (after the action of strong sulphuric acid) was boiled three hours longer, and examined as before. It did not need to be decolorised. That it had suffered considerable alteration was shown by the fact that it now gave quasi-$[\alpha]_D = 64°49'$, and 28·27 per cent of dextrose calculated on the dry residue, or 22·45 per cent calculated on the dry wood. After evaporating to dryness, and treating with cold, strong alcohol, the matter not readily dissolved in this liquid gave quasi-$[\alpha]_D = 58°66'$, while the portion soluble in alcohol gave quasi-$[\alpha]_D = 49°85'$, both calculated as dextrose.

It should be said that most of these experiments with birch wood were made before those upon maple wood, as reported above. It is evident enough that beside xylose and dextrose some other substance of higher rotatory power than dextrose is produced when birch wood is boiled with acids under the conditions here described.

(To be continued).

A NEW COLOUR REACTION FOR AMYGDALIN.

By E. R. DEACON.

During some experiments I was conducting recently on amygdalin I found that on treating the substance with a few drops of concentrated sulphuric acid a bright carmine colour was developed, which was discharged on pouring into water.

I cannot find this reaction mentioned in the books, and the above colour reaction may interest your readers.

Two samples of amygdalin from presumably different sources gave the same characteristic colour.

Chemical Laboratory,
Technical College, Finsbury, E.C.
June 5th, 1901.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 3rd inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Mr. Henry J. Wood and Mr. John T. Middlemore, M.P., were elected Members.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Extraordinary General Meeting, May 15th, 1901.

Prof. Emerson Reynolds, Sc.D., F.R.S., President, in the Chair.

The President stated that this Meeting had been convened in accordance with a requisition, signed by sixty-six Fellows of the Society, to consider the decision of the Council to hold the Ordinary Meetings of the Society during the ensuing session on Wednesdays at 5.30 p.m.

After a discussion in which, amongst others, the following Fellows took part, Dr. Lewkowitsch, Dr. Moody, Mr. A. G. Bloxam, Mr. Cassal, Dr. Armstrong, Mr. Hehner, Mr. Tyrer, Mr. Fakes, Prof. Tilden, Prof. Ramsay, Dr. Crossley, Dr. Forster, Prof. Dewar, and Mr. F. J. Lloyd,

Dr. Armstrong moved and Mr. Hehner seconded the following resolution :—

"That in the opinion of this Meeting the change proposed in the day and hour of meeting will prevent the attendance of a large proportion of the junior and other Fellows who have hitherto been regular attendants; that the said change is contrary to the best interests of the Society, and that it is desirable that the question be reconsidered by the Council."

The resolution was declared by the President to be carried. The numbers being asked for, a division was taken, with the following result :—For the resolution, 92; against, 3. A certain number of Fellows abstained from voting.

Ordinary Meeting, May 16th, 1901.

Prof. Emerson Reynolds, Sc.D., F.R.S., President, in the Chair.

Messrs. McKenzie, Ferguson, Woodbridge, Robertson, Jennings, Dodd, Neil, Mees, Wayland, and Dixon were formally admitted Fellows of the Society.

The following certificates were read for the first time:—Hubert Haigh Barker, 3, Waverley Place, St. John's Wood, N.W.; George Dean, 2, Scriven Grove, Knaresborough; Thomas Henry James Eling, 32, Hill Top Avenue, Shepherd's Lane, Leeds; Edward Kenneth Hanson, Hadley Wood, N.; Frederick Thomas Harry, 106, Sandmere Road, Clapham, S.W.; Edward Horton, 8, Orford Street, Chelsea, S.W.; Christopher George Kiddell, 24, Queen's Gardens, Muswell Hill, N.; Robert Tabor Lattey, Trinity College, Oxford; F. G. Macdonald, Government Laboratory, Durban; Frank Oram, Market Place, Romsey; John Edward Purvis, University Chemical Laboratory, Cambridge; Gerald Theodore Sylvester Sichel, R.N. Hospital, Haslar, Gosport; Duncan Randolph Wilson, Magdalen College, Oxford.

The President read the resolution passed at the Extraordinary General Meeting, which, he stated, had been that afternoon brought before the Council, by whom it was being carefully considered.

Dr. Armstrong, referring to the ruling given by the President at the previous meeting, that a paper read in the absence of the author could not be discussed, drew attention to By-law XIV., and contended that this By-law expressly provided that every paper communicated to the Society should be open to discussion. He stated that during the whole course of his experience, extending over thirty years, it had always been the practice of the Society, when the occasion arose, to discuss papers read in the absence of their authors.

Dr. PERKIN, in reply to a question by Dr. Armstrong, said that in the past papers had often been discussed in the absence of their authors.

Dr. DIVERS said that having been resident in Japan when most of his papers were sent to the Society, he had always been willing that they should be discussed.

Prof. DUNSTAN pointed out that By-law XIV. evidently supposed that authors would be present to read their papers, and its directions could not be literally followed at the present time. In these matters, however, the By-law gave large discretion to the Chairman.

Mr. W. P. BLOXAM asked whether it was within the power of the President to closure or prevent discussion on any paper read to the Society.

The PRESIDENT replied that, as a general rule, he should not think of doing so.

Mr. BLOXAM remarked that probably Dr. Armstrong would recollect when he read a paper on ammonium sulphides, Dr. Armstrong, as President, had prevented any discussion whatever on that paper.

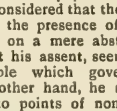
The PRESIDENT considered that the By-law read by Dr. Armstrong assumed the presence of the author at the meeting. Criticism on a mere abstract in the author's absence, and without his assent, seemed contrary to the fair general principle which governed most public meetings. On the other hand, he saw no objection to questions relating to points of nomenclature or detail which could be elucidated by reference to the original paper, should the latter be available at the time.

Dr. ARMSTRONG said that such being the President's opinion, and as he could not accept the ruling as correct, it would be necessary for him to raise the question again elsewhere.

Of the following papers, those marked * were read:—

*78. "*Derivatives of Methylfurfural.*" By H. J. H. FENTON and Miss M. GOSTLING.

The authors have already (*Trans.*, 1898, lxxiii., 554; 1899, lxxv., 423; 1901, lxxix., 361) described the isolation, properties, and constitution of bromomethylfurfural,—



a well-defined crystalline substance, melting at 60°, which gives rise to remarkable colour reactions. Because of the interest which attaches to this compound, owing to its relations with the carbohydrates and the bearing of its formation on questions in plant physiology, it was considered desirable to make a further study of the compound and its derivatives. The following new compounds were described:—

Chloromethylfurfural, m. p. 36—37°; *acetoxy*-derivative, m. p. 55°; *benzoxy*-derivative, m. p. 56—57°; *difurfurylethane-dialdehyde*, m. p. 119—120°; with its corresponding *dihydrazone*, m. p. 179—181°; *dicarboxylic acid*, m. p. 267—269°; and *dioxime*, m. p. 182°. A very simple method of obtaining pure methylfurfural was also described.

DISCUSSION.

Mr. W. J. POPE asked whether bromomethylfurfural, which contains a bromine atom and an ethereal oxygen atom attached to adjacent carbon atoms, was capable of condensing with alkyl sulphides or tertiary amines to yield sulphonium or quaternary ammonium derivatives.

Mr. FENTON, in reply, said that both the chloro- and the bromo-derivatives of methylfurfural readily interacted with various amines.

*79. "*Optically Active Nitrogen Compounds and their Bearing on the Valency of Nitrogen; Dextro- and Lævo-α-benzylphenylallylmethylammonium Salts.*" By W. J. POPE and A. W. HARVEY.

The authors have prepared in a state of purity a number of substances owing their optical activity to the presence of an asymmetric pentad nitrogen atom.

The externally compensated α-benzylphenylallylmethylammonium iodide of Wedekind, when treated with silver *d*-camphorsulphonate, yields *d*-benzylphenylallylmethylammonium *d*-camphorsulphonate, which melts at 171—173° and has the molecular rotation $[M]_D = +218{\cdot}1°$ in an aqueous solution containing one-fifth of a grm.-molecule per litre; whence the value for the *d*-benzylphenylallylmethylammonium ion is $[M]_D = +166{\cdot}4°$. The residue from the preparation of this salt, when treated in aqueous solution with potassium iodide, yields crude *l*-benzylphenylallylmethylammonium iodide, which, on treatment with silver *l*-camphorsulphonate, gives the new salt *l*-*benzylphenylallylmethylammonium l-camphorsulphonate*. This melts at 171—173°, and has the molecular rotation $[M]_D = -210{\cdot}6°$ in an aqueous solution containing one-fourth of a grm.-molecule per litre; the molecular rotation $[M]_D = -159{\cdot}0°$, is thence deduced for the ion of the *l*-base.

These salts, when treated with potassium iodide in aqueous solution, give crystalline precipitates of the corresponding iodides which may be crystallised from alcohol without undergoing inversion; they are soluble in cold chloroform, and in this solvent have the specific rotations $[\alpha]_D = +55{\cdot}2°$ and $[\alpha]_D = -53{\cdot}4°$ respectively. On warming the chloroform solutions, the rotation rapidly vanishes, and a similar result is attained on allowing the cold chloroform solutions to stand for three days; the solutions on evaporation yield the externally compensated iodide in a state of purity, so that the inversion may be attributed to a dissociation into tertiary base and benzyl iodide.

The bromides are prepared in a similar manner and have the specific rotations $[\alpha]_D = +64{\cdot}1°$ and $[\alpha]_D = -65{\cdot}0°$ respectively in cold chloroform; the salts undergo inversion in chloroform, just as the iodides do, although appreciably less rapidly.

d-*Benzylphenylallylmethylammonium nitrate*,—

$$C_7H_7{\cdot}N(C_6H_5)(C_3H_5)(CH_3)NO_3,$$

is a colourless crystalline substance melting at 164—165°, and in aqueous solution has the molecular rotation $[M]_D = +165{\cdot}3°$, a value comparing well with that of the ion of the *d*-base deduced from the examination of the *d*-camphorsulphonate.

d-*Benzylphenylallylmethylammonium mercuri-iodide*, $C_7H_7{\cdot}N(C_6H_5)(C_3H_5)(CH_3)I,HgI_2$, is obtained as a bright yellow crystalline compound by heating the pure *d*-iodide with one equivalent of mercuric iodide in ethyl acetate solution; it melts at 125—127°, and has the specific rotation $[\alpha]_D = +24{\cdot}4°$ in ethyl acetate solution. The enantiomorphously related salt also melts at 125—127°, and has the specific rotation $[\alpha]_D = -23{\cdot}0°$ in ethyl acetate. It is concluded that these mercuri-iodides contain quinquevalent nitrogen.

Attention was drawn to the persistency of the optical activity of these asymmetric nitrogen compounds except under the specific conditions which cause inversion. It should be noted that these substances are fundamentally distinguished from asymmetric carbon compounds in that they are electrolytes which, in aqueous solution, must be supposed to undergo electrolytic dissociation, giving an optically active ion of which the disrupted valency is one of those attached to the asymmetric atom; yet even under these conditions no inversion takes place.

DISCUSSION.

Dr. ARMSTRONG said that when Messrs. Pope and Peachey first stated that they had succeeded in obtaining optically active nitrogen compounds, he had pointed out that the discovery was of special importance, because it seemed at last to afford a means of deciding the long standing dispute as to the valency of nitrogen in the ammonium compounds. The discovery was not in itself sufficient to disprove the molecular hypothesis advocated by Kekulé, as it was possible to formulate the ammonium

salts as molecular compounds, which it was conceivable might have a tetrahedral configuration. But the subsequent discovery of optically active sulphur compounds by Messrs. Pope and Peachey might be regarded as complete disproof of the molecular compound hypothesis, and it was consequently legitimate to argue that nitrogen acted as a pentad in the ammonium compounds. Nevertheless, there could be little doubt that the "superior" valency assumed by nitrogen in the ammonium compounds and by sulphur in the sulphonium compounds was in some way different in character from the lower or ordinary valency of these elements: that it was a "conditional" valency, as nitrogen became pentad, and sulphur tetrad only under special conditions, and in a very limited number of cases. There could be little doubt that the direction in which valency could act was of importance, and the inquiry into this must play an important part in the future. Reference was made to the behaviour of sulphur in thiophen as affording proof that the superior valency in some way became masked by the inclusion of the sulphur in the ring. The use made by the authors of the behaviour of double mercuric and platinic compounds as arguments against a change in valency was of a most ingenious character, as was also the reference to the evidence afforded by the stability of the active salts against the ionic dissociation hypothesis: the suggestion that a free affinity could not well act "materially," and serve to condition optical activity, was particularly worthy of note.

Dr. Hewitt referred to Mr. Pope's remarks on the fact that the addition of mercuric iodide to optically active quaternary ammonium iodides gives rise to double salts in which the optical activity is preserved, and the conclusion drawn that the valency of nitrogen remains unchanged, and the extension of this argument to the valency of sulphur in the compounds of sulphonium iodides with metallic iodides. He considered it possible that the two active forms of a sulphonium iodide might add on mercuric iodide, the sulphur atom becoming hexavalent, and nevertheless the two resulting octahedral formulæ be related to one another as an object is to its image.

Dr. Forster suggested that the numerical difference between the rotation constants of *d*A*d*B and *l*A*l*B might disappear if *l*A*l*B were separated first, by adding *l*-camphorsulphonate to the racemic mixture, and inquired whether *l*-bromocamphorsulphonic acid would not be a useful substitute for *l*-camphorsulphonic acid. He questioned whether racemisation of the active ammonium iodide is due to dissociation on the lines indicated by Mr. Pope, pointing out that addition of ammonia should accelerate the change. Referring to the principle that a change of valency involves an alteration in the original valency directions, he wished to know why, if divalent sulphur forming part of a ring is prevented from becoming tetravalent on account of this principle, nitrogen does not lie under the same disability.

Dr. H. McKenzie asked whether Mr. Pope had had occasion to confirm Le Bel's resolution of inactive methylethylpropylisobutylammonium chloride by means of *Penicillium glaucum*; and, further, whether he had attempted to resolve Le Bel's substance by aid of an optically active acid, such as α-bromocamphorsulphonic acid.

Dr. Morgan, in supporting the view that the nitrogen in the ring systems of the pyridine and acridine types is generally capable of assuming the quinquevalent condition, recalled the fact that naphthacridine readily combines with alkyl iodides, yielding quaternary iodides so stable that they can be crystallised from hot aniline without decomposition, indicating thereby that the cyclic nitrogen is able to maintain its quinquevalency, even in the presence of an amine containing a nitrogen atom free from constraint as regards the direction of its linkings.

Mr. W. J. Pope, in reply, observed that the new principle brought forward, namely, that during change of valency of an atom the valency directions might also change, appeared to be applicable when a bi- or quadrivalent sulphur atom became quadri- or sexa-valent respectively, or when a quinquevalent nitrogen atom became septavalent; it is not necessarily applicable to the case of a tervalent nitrogen becoming quinquevalent because such a change might be effected by the two fresh groups attaching themselves to the nitrogen atom along a direction perpendicular to the plane containing the original three groups. The principle derived support from the fact that bivalent sulphur contained in a closed ring, and consequently restrained from altering its environment, cannot be caused to combine with alkyl iodides, and become quadrivalent; the *n*-alkyl derivatives of piperidine and tetrahydroquinoline, on the other hand, combine with alkyl iodides at least as readily as do tertiary bases in which the nitrogen atom is not contained in a closed ring. *d*-Benzylphenylallylmethylammonium iodide undergoes inversion in chloroform solution about twice as rapidly as the corresponding bromide, but no experiments have yet been made with other salts. It is not immediately apparent how the inversion of optically active stannomethyl derivatives can be caused by dissociation, but the inversion is possibly due to dissociation of the stannic compound into a stannous compound and an alkyl salt.

*80. "*Reactions of Hydroxyoxamides.*" By R. H. Pickard and W. Carter.

Hydroxyoxamide and its mono-phenyl, *p*-tolyl, α- and β-naphthyl-derivatives, $RNH{\cdot}CO{\cdot}CONHOH$, react as hydroxamic acids. The general reactions of hydroxamic acids (Thiele and Pickard, *Ann.*, 1899, cccix., 189), can be carried out with these compounds, giving quantitative yields of substituted biurets, carbonyl di-carbamids, and allophanates.

The monosubstituted phenyl-, *p*-tolyl-, α-, and β-naphthyl-biurets, analogously substituted ethyl allophanates, and the *sym*-disubstituted carbonyl di-carbamides, $CO(NHCONHR)_2$, were described.

The acetate of oxalodihydroxamic acid described by Hantzsch (*Ber.*, 1894, xxvii., 801), is apparently a diacetate; it is acid in properties, and dissolves in a solution of sodium carbonate, giving a solution which, after warming, contains small quantities of hydrazine.

*81. "*The* sym*-Trichlorobromoanilines; and Chloro- and Bromoamino-derivatives of Chlorobromoacetanilides.*" By F. D. Chattaway and K. J. P. Orton.

The authors called attention to the great resemblance existing between the two similarly constituted *sym*-chlorodibromoanilines and their acetyl derivatives respectively. There is a similar resemblance between the two *sym*-dichlorobromoanilines. The acetylchloroamino-derivatives, however, serve to distinguish the one isomeric aniline from the other, as they possess melting points lying several degrees apart.

The following compounds have been prepared:—*4-Chloro-2:6-dibromoaniline*, $C_6H_2ClBr_2{\cdot}NH_2$ (first prepared by Hofmann, *Ann.*, 1845, liii., 38), needles, melting at 97° (Hofmann does not record the melting point), and boiling at 301° under 760 m.m. pressure; *4-chloro-2:6-dibromoacetanilide*, $C_6H_2ClBr_2{\cdot}NHAc$, flattened prisms or needles, melting at 226—227°; *acetylchloroamino-4-chloro-2:6-dibromobenzene*, $C_6H_2ClBr_2{\cdot}NClAc$, short, four-sided prisms melting at 110—111°; *2-chloro-4:6-dibromoaniline*, $C_6H_2ClBr_2{\cdot}NH_2$ (first prepared by Langer, *Ann.*, 1882, ccxv., 115), needles, closely resembling the isomeric aniline, and melting at 95°; *2-chloro-4:6-dibromoacetanilide*, $C_6H_2ClBr_2{\cdot}NHAc$, flattened prisms or needles, melting at 227°; *acetylchloroamino-2-chloro-4:6-dibromobenzene*, $C_6H_2ClBr_2{\cdot}NClAc$, four-sided prisms, melting at 99—100°; *2:6-dichloro-4-bromoaniline*, $C_6H_2Cl_2Br{\cdot}NH_2$ (first prepared by Fittig and Büchner, *Ann.*, 1877, clxxxviii., 22), needles, melting at 92° (Fittig and Büchner give 93·5°); *2:6-dichloro-4-bromoacetanilide*, $C_6H_2Cl_2Br{\cdot}NHAc$, flattened prisms or needles, melting at 214°; *acetyl chloroamino-2:6-dichloro-4-bromobenzene*, $C_6H_2Cl_2Br{\cdot}NClAc$, prisms melting at 81°; *2:4-dichloro-6-bromoaniline*,

$C_6H_2Cl_2Br{\cdot}NH_2$, needles melting at 83·5°; 2 : 4-*dichloro*-6-*bromoacetanilide*, $C_6H_2Cl_2Br{\cdot}NHAc$, flattened prisms or needles melting at 218°; *acetylchloroamino*-2 : 4-*dichloro*-6-*bromobenzene*, $C_6H_2Cl_2Br{\cdot}NClAc$, four-sided prisms melting at 91—92°; 2 : 6 - *dibromoacetanilide*, $C_6H_3Br_2{\cdot}NHAc$, prisms melting at 208—209°; *acetylchloroamino*-2 : 6 *dibromobenzene*, $C_6H_3Br_2{\cdot}NClAc$, short prisms melting at 88°; *acetylbromoamino*-4-*chlorobenzene*, $C_6H_4Cl{\cdot}NBrAc$, yellow plates, melting at 91°; *acetylchloroamino*-4-*bromobenzene*, $C_6H_4Br{\cdot}NClAc$, rhombs, melting at 108—109°; *acetylbromoamino*-2 : 4-*dichlorobenzene*, $C_6H_3Cl_2{\cdot}NBrAc$, yellow plates or prisms, melting at 95—96°; *acetylchloroamino*-4-*chloro*-2 *bromobenzene*, $C_6H_3ClBr{\cdot}NClAc$, four-sided prisms, melting at 74—75°; *acetylbromoamino* - 4 - *chloro* - 2 - *bromobenzene*, $C_6H_3ClBr{\cdot}NBrAc$, yellow rhombs melting at 85—86°; *acetylchloroamino* - 2 - *chloro* - 4 - *bromobenzene*, $C_6H_3ClBr{\cdot}NClAc$, rhombs or prisms melting at 88—89°; *acetylbromoamino* - 2 - *chloro* - 4 - *bromobenzene*, $C_6H_3ClBr{\cdot}NBrAc$, yellow, four-sided prisms melting at 110—111°; *acetylchloroamino* - 2 : 4 - *dibromobenzene*, $C_6H_3Br_2{\cdot}NClAc$, plates or rhombs melting at 56—57°; *acetylchloroamino* - 2 : 4 : 6 - *tribromobenzene*, $C_6H_2Br_3{\cdot}NClAc$, prisms melting at 109—110°.

*82. "*Replacement of Bromine by Chlorine in Anilines.*" By F. D. Chattaway and K. J. P. Orton.

When tribromoaniline (NH_2 : Br : Br : Br = 1 : 2 : 4 : 6) reacts with acetylchloroamino-2 : 4-dichloroacetanilide in chloroform solution, bromine is evolved, and in addition to an azo-derivative and another coloured substance, a chlorodibromoaniline can be isolated. This aniline proves to be 4-chloro-2 : 6-dibromoaniline. With *sym*-chlorobromoaniline (2 chloro-4 : 6-dibromoaniline, 4-chloro-2 : 6-dibromoanilines, 2 : 4-dichloro-6-bromoaniline, and 2 : 6-dichloro-4-bromoaniline), it was observed that bromine was given off to a far greater extent from those anilines which possessed a bromine atom in the para-position relatively to the amino-group. Again, an aniline in which bromine had been replaced by chlorine could only be isolated in the case of those anilines where bromine originally occupied the para-position. Thus, 2 : 4-dichloro-6-bromoaniline could be obtained from 2-chloro-4 : 6-dibromoaniline, but not from 4-chloro-2 : 6-dibromoaniline.

Acetylchloroamino-2 : 4 : 6-tribromobenzene (and similar derivatives of chlorobromobenzenes) gives off bromine when heated in a sealed tube with acetic acid. No pure chlorobromoacetanilide has been isolated.

*83. "*The Absorption Spectra of Cyanogen Compounds.*" By W. N. Hartley, F.R.S., J. J. Dobbie, D.Sc., M.A., and A. Lauder, B.Sc.

The authors described the results of an examination of the absorption spectra of cyanogen compounds, more particularly of cyanuric acid, melamine, and their respective esters.

Cyanuric acid and methyl cyanurate (m. p. 135°) are commonly represented as closed chain compounds in which the chain is formed of alternate atoms of carbon and nitrogen alternately doubly and singly linked, while methyl *iso*cyanurate (m. p. 175°) is represented as a derivative of *iso*cyanuric acid containing three keto-groups and having the carbon and nitrogen atoms only singly linked. From the circumstance that pyridine, dimethylpyrazine, and other similar substances, in which the carbon and nitrogen atoms are united by alternate double and single linkings, exhibit strong absorption bands, it was expected that cyanuric acid and its esters would likewise exhibit marked selective absorption. On the other hand, it was anticipated that the esters of *iso*cyanuric acid would behave like piperidine and other substances composed of a closed chain of singly linked carbon and nitrogen atoms. The authors found, however, no trace of selective absorption in any of the substances examined, and pointed out that in the absence of more satisfactory chemical evidence it is questionable whether the constitution of cyanuric acid ought to be represented by a structural formula so closely analogous to that of pyridine and of dimethylpyrazine.

The spectrographic examination confirms the view generally accepted on the evidence of chemical reactions, that cyanuric acid and methyl cyanurate (m. p. 135°) are similarly constituted, and that the relations between melamine and triethylmelamine (m. p. 74°) are correctly represented by the commonly accepted formulæ.

84. "*The Nutrition of Yeast.*" Part III. By A. L. Stern, D.Sc.

The author has determined the effect of varying the concentration of the sugar, the temperature of fermentation, the amount of seed-yeast and the time, on the nutrition of yeast.

The experiments were made in exactly the same manner as those previously described (*Trans.*, 1899, lxxv., 202); the sugar used was dextrose, the nitrogenous nutriment, asparagine; and the inorganic nutriment, potassium phosphate, magnesium sulphate, and calcium sulphate; and the yeast a pure culture from a Burton pitching yeast.

The conclusions drawn are:—

(1). Any increase of nitrogenous or inorganic nutriment beyond a definite limit will not increase either the amount of nitrogen assimilated by the yeast, or the weight of the yeast. This limit is but little greater than the largest amount which the yeast is able to assimilate under the conditions of the experiment.

(2). Any increase of the sugar is accompanied by an increase of the weight of nitrogen assimilated, and of the weight of the yeast. This increase goes on up to the strongest concentrations which can be completely fermented. The rate of increase is greatest at the lowest concentrations, and falls off gradually as the concentration rises.

(3). Temperatures between 12° and 25° have but little influence on the weight of nitrogen assimilated and the weight of the yeast crop. At higher temperatures reproduction is weakened.

(4). The weight of the nitrogen assimilated and of the yeast crop is composed of two quantities: the weight of the seeding plus a quantity dependent on the composition of the solution.

(5). The growth of the yeast is during a portion of the fermentation proportional to the amount of sugar fermented, and proceeds as long as any sugar remains unfermented.

From a consideration of these deductions, and of the work of others, the author concludes that there is an essential difference between the functions of the inorganic and nitrogenous nutriment on the one hand, and of the sugar on the other; that the former supply only material to the yeast, whilst the latter supplies both material and energy. Whether fermentation is caused by an enzyme or not, the author does not yet consider definitely determined; whilst there is certain amount of evidence to support this supposition, there is none to negative it.

85. "*On the Colloid Form of Piperine, with especial reference to its Optical Refraction and Dispersion.*" By H. G. Madan.

The author has examined the conditions under which crystalloid piperine is converted into the colloidal allotropic form of the substance. He finds that while crystallised piperine when heated to its melting point, 135°, solidifies on cooling into a transparent resin-like substance, the latter, when thus prepared, is not permanent, but reverts spontaneously in the course of a few months into the crystalloid form. The same change takes place quickly and completely when the substance is heated to 100°. If, however, piperine is kept for an hour at a temperature of 180°, the resulting product is much more stable if not absolutely permanent as a colloid. It does not become crystalline when heated to 100° or above, nor has the lapse of two and a half years had any effect in changing it back into the crystalloid condition.

The results of a determination of the refractive indices of colloid piperine for some of the principal spectrum lines were given, from which it appears that, while its refraction is very high ($\mu_D = 1{\cdot}684$), its dispersion is quite extraordinary, the visual spectrum being nearly four times as long as that given by a prism of dense flint glass having the same refracting angle. The coefficient of dispersion ($\mu H_\gamma - \mu H_\alpha$) is 0·142, while that of carbon disulphide is only 0·057.

86. "*Note on Pyromucylhydroxamic Acid.*" By R. H. Pickard and A. Neville.

The reactions of pyromucylhydroxamic acid have been studied with a view of obtaining the furan carbamides and carbamates by the method of Thiele and Pickard. These are, however, uncrystallisable oils, which decompose on hydrolysis. *Pyromucylhydroxamic acid*, $C_4H_3O{\cdot}CONHOH$, obtained by hydrolysing ethyl pyromucate with hydroxylamine, melts at 124°, and forms a *benzoyl* derivative, which melts at 134°.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, May 31st, 1901.

Prof. S. P. Thompson, President in the Chair.

A paper "*On the Resistance of Dielectrics and the Effect of an Alternating Electromotive Force on the Insulating Properties of India-rubber,*" by A. W. Ashton, was read by Prof. Fleming.

The author has obtained from his experiments formulæ for the charging and discharging currents of a condenser with rubber dielectric. The currents are exponential functions of the time. Curves for various potential differences have been plotted, and were exhibited. These curves show that the insulating properties of rubber are increased by the application of high alternating electromotive forces.

Prof. Fleming then read a note by Mr. Ashton "*On the Electrification of Dielectrics by Mechanical means.*"

A sheet of pure Para rubber was placed in a condenser, the plates of which were connected to a quadrant electrometer. A two-pound weight was then dropped on to the condenser from a height of three inches. The electrometer received two impulses of opposite sign, one quickly following the other. The rubber was then stretched while in position, and a potential difference of seven volts was shown between the plates, the top plate being negative. The condenser and electrometer were then discharged, the sheet reversed, and the experiment repeated. The same effect was produced, the top plate again being negative. It appears, therefore, that polarisation of a dielectric being thus produced by mechanical energy, some part of the mechanical energy expended on the india-rubber during manufacture would remain in the dielectric as electric energy.

A Model which Imitates the Behaviour of Dielectrics, by Prof. Fleming and Mr. Ashton, was exhibited by Prof. Fleming.

The behaviour of dielectrics with regard to their residual charge is analogous to that of wires subjected to mechanical stress. A simple twisted wire is not, however, able to imitate all dielectric effects, and the present paper describes a model which represents things more completely. Six pistons separated by springs are placed inside a vertical cylinder. The bottom piston fits fairly tightly in the cylinder. The second piston fits slacker than the first. The third piston has a small hole in it, and each succeeding piston has a greater area cut away, the top piston having just sufficient metal left to make the spring come to rest without vibration after being compressed. The cylinder is filled with machine-oil and vaseline. To the top piston is attached a rod by means of which pressures can be exerted on the pistons for any length of time. This represents the charging of the condenser. The motion of the rod after releasing the weights represents the discharge of the condenser. This is registered graphically by a revolving drum, and the curves obtained are very similar to those from condensers with dielectrics.

Prof. Ayrton said he would like to know in what respect the model shown was superior to a strained wire. He had noticed about ten years ago that alternating E.M.F.'s appeared to improve condensers. He was then working with comparatively small voltages, and he was interested to know that Mr. Ashton, working with high voltages, had established the improvement. The deflection obtained by stretching the india-rubber sheet might be due to changes in temperature, the dielectric having a high thermoelectric power.

Mr. Price was glad that the question as to what actually might be called the resistance of a dielectric had been raised. There are two theories of residual charge; one due to Maxwell and the other to Heaviside. The model exhibited represents Maxwell's theory. He considered that the electrometer experiment with the rubber dielectric favoured Heaviside's theory; that is that the dielectric is composed of small charged bodies similar to the small magnets conceived to constitute a magnet. He expressed his interest in the fact that the top plate of the condenser was always negative.

Mr. Blakesley suggested putting a small hole in the bottom piston of the model so that it might represent a condenser passing a small steady current. With regard to the stretched rubber experiment, he said it would be interesting to make observations with the plates of the condenser vertical.

Mr. Campbell said he had made experiments, and found that the change in capacity of the rubber condenser affects the voltage sufficiently to mask the real effect.

Mr. Appleyard said it was important to have perfect contact between the dielectric and the metal plates.

It was pointed out by a visitor engaged in the cable industry that manufacturers are aware that pressure affects the insulating properties of gutta-percha. Rubber is a mixture, and different rubbers behave differently under the action of alternating potential differences.

The Chairman said that if the quantity of electricity taken in on charging was equal to the quantity given out on discharge then there could be no dielectric hysteresis.

The Society then adjourned until June 14th.

CORRESPONDENCE.

FIRES AT CHEMICAL WORKS.

To the Editor of the Chemical News.

Sir,—It is satisfactory to learn that, although several explosions occurred at the recent fire at Runcorn, no person was injured. But, in view of the possible loss of life of which fires at chemical works are liable to be the cause, it is important, in the interests of common humanity, that no expense should be spared to fit such premises with absolutely the best fire-extinguishing and life-saving apparatus.

I have been gratified to notice that several of the leading firms in the trade take an interested view of the question—such as Messrs. Brunner, Mond, and Co., the United Alkali Co., and Messrs. Lever Bros., at Port Sunlight—and are provided with portable steam fire-engines by the Merryweather firm; besides which, they possess private fire brigades, thereby ensuring the efficient use of the apparatus in case of fire. These arrangements must be advantageous, even from the economical point of view; and the subject is worthy of increased attention by the proprietors of chemical works in its humanitarian aspect.—I am, &c.,

The Editor of *The Fireman.*

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxii., No. 19, May 13, 1901.

Aromatic Organo-magnesium Compounds.—MM. Tissier and Guignard.—The halogen derivatives of benzene and its homologues react easily on magnesium, with formation of organo-metallic compounds analogous to those of the fatty series. The method employed is the same for both. Monobromobenzene and monobromotoluene are made to drop slowly on to magnesium, and, after the addition of some anhydrous ether, the corresponding organo-metallic derivative is produced: C_6H_5—Mg—Br and $C_6H_4(CH_3)$—Mg—Br. A portion of this compound crystallises from the ether at ordinary temperatures, and on cooling down to freezing-point the whole becomes solid. At the beginning of the operation, the vessel in which the preparation takes place should be slightly heated, or a small particle of iodine added to start the reaction; after this it proceeds regularly. An investigation of the various reactions shows that the halogen ethers of the aromatic series react on magnesium in an exactly similar manner to the ethers of the fatty series, but the velocity of the reaction diminishes with the complication of the radicle.

The Phosphoric Acid of the Soil.—Th. Schlœsing, jun.—The author extracts all the phosphoric acid in the form of phosphates which are soluble in water from the soil at Boulogne, Joinville, and Neauphle, and examines these. He also uses, on the same soils, very dilute nitric acid, and obtains different quantities of soluble phosphates.

MEETINGS FOR THE WEEK.

THURSDAY, 13th.—Royal Society, 4.30. (The Bakerian Lecture). "The Nadir of Temperature, and Allied Problems—(1) Physical Properties of Liquid and Solid Hydrogen; (2) Separation of Free Hydrogen and other Gases from Air; (3) Electric Resistance, Thermometry, and the Boiling-point of Hydrogen; (4) Experiments on the Liquefaction of Helium at the Melting-point of Hydrogen; (5) Pyro-electricity, Phosphorescence, &c.," by James Dewar, M.A., LL.D., F.R.S.

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THE CHEMICAL NEWS.

Vol. LXXXIII., No. 2168.

CONCERNING THE INFLUENCE OF SELENIUM ON CERTAIN TESTS FOR ARSENIC.

By OTTO ROSENHEIM, Ph.D., F.C.S.,
Research Scholar in Pharmacological Chemistry, King's College.

In view of the fact that the presence of selenium compounds has recently been demonstrated in brewing-sugar and in two samples of beer implicated in the beer-poisoning epidemic in Manchester, the chemistry of this substance becomes invested with greater practical interest than heretofore. This is more especially the case since the highly poisonous nature of selenium compounds has been placed beyond any doubt (Tunnicliffe and Rosenheim, *Lancet*, Feb. 2, 9, and March 30, 1901).

The fact that selenium, as far as the products in question are concerned, was accompanied by arsenic, introduces a complication. From the point of view of the analyst, the question becomes not merely one of the detection of selenium or arsenic alone, but of the detection of selenium in the presence of arsenic and *vice versâ*.

Since selenium has been brought into the region of practical hygiene, much has been said and written concerning its chemical behaviour. Many, apparently contradictory, statements have been recorded, owing no doubt to the scarcity and inaccessibility of the literature. Under these circumstances, the following observations, although in some part consisting of a critical repetition of the work of former investigators, would seem to be of some interest.

1. *Behaviour of Selenium in Marsh's Test.*

If selenium compounds be submitted to the Marsh test (the apparatus being provided with a small wash-bottle containing about 50 c.c. of a 5 per cent lead acetate solution), as for the exact estimation of arsenic,* it will be observed that no deposit is produced in the heated glass tube, even when quantities of 100 m.grms. selenious acid are treated for two hours. The zinc in the generating vessel, however, assumes an unusual appearance, becoming covered with a brick-red deposit of amorphous selenium. The small quantities of hydrogen selenide, evading reduction by the zinc, are completely retained by the lead solution, lead selenide being formed and deposited. If, however, the lead acetate wash-bottle be omitted, a deposit of selenium is obtained in the glass tube at some distance from the heated part.† This deposit varies in colour from dark brick-red to reddish yellow, according to the quantities used (and the relative freedom from sulphur and carbon compounds of the zinc employed). It is possible, by using a tube of very small diameter (1 m.m.), to obtain a distinct deposit from one-tenth m.grm. selenious acid (=0·06 m.grm. Se). The actual amount of selenium thus deposited is, however, very small, owing to the ease with which hydrogen selenide is decomposed, even in aqueous solution, and reduced to selenium in the generating vessel. By a quantitative estimation, it was shown that 96 per cent of the selenium introduced as selenious acid was retained by the zinc.*

The systematic study of the influence of selenium compounds on the formation of the arsenical mirror in the absence of a lead acetate wash-bottle brings out clearly two facts which do not seem to have been sufficiently emphasised in recent publications (compare Willcox, *Lancet*, March 16, 1901; Berry, *Journ. Soc. Chem. Ind.*, vol. xx., 322 and Discussion). It may be pointed out at once that both these facts have been observed already by L. Dawydow (*Farmazeft*, 1895, iii., 1; abstracted in *Chem. Zeit., Analyst, Chem. Soc. Journ.*, &c.), and have since, according to private information, been confirmed by several other observers in this country, apparently without the knowledge of Dawydow's experiments.

The first fact is important with regard to the detection of arsenic; and is, that selenium compounds have a very distinct inhibitory influence on the formation of the arsenical mirror, and under certain conditions completely prevent its formation.† *Ceteris paribus*, the influence is proportional to the amount of selenium present; this is best shown by the accompanying figure (Fig. 1), which is an exact reproduction of the results actually obtained.

The tests were made under exactly identical conditions —the same quantity of zinc from one stock and a generating vessel of the same size (250 c.c.) being used for each experiment. The zinc was relatively free from sulphur.‡ In order to control the evolution of hydrogen more exactly than by the size of the flame, and thus to obtain comparable results, a small wash-bottle was used at the end of the apparatus, and the acid supply regulated by means of a stopcock in the sulphuric acid funnel. The time for each experiment was one hour, the tube being heated a quarter of an hour previously, to make sure of the absence of arsenic in the materials used. The quantity of arsenic was 1 m.grm. in all experiments, whilst the quantity of selenious acid varied from 0·3 to 20 m.grms. The deposit formed on the zinc in the generating vessel in the presence of arsenic and selenium was of a dark reddish brown colour. In the case of Experiment 9, the evolution of hydrogen was kept very slow, with the result that only the faintest deposit was obtained. For the sake of comparison, one experiment was made under identical conditions with 20 m.grms. selenious acid alone. From this the usual selenium deposit was obtained.

The second fact to be observed is of importance with regard to the detection of selenium, and consists in the total absence of any brick-red colour in the deposits obtained from admixtures of arsenic and selenium in Marsh's apparatus. Just as in the formation of the ordinary arsenical mirror, so in this case, a slight anterior brownish portion, followed by a metallic black portion, may be observed in the first half-hour of the experiment. After one hour, however, the two mirrors are united into one black

* Compare Polenske, *Arbeiten a. d. k. Gesundheitsamte*, v., 357; Kuhn u. Sager, *Ber. d. Deut. Chem. Ges.*, xviii., 1758; Langmuir, Chemical News, 1899, vol. lxxix., p. 121 (from *Journ. Am. Chem. Soc.*). The use of this wash-bottle is indispensable for arsenic estimations, and its value has been clearly brought out by the experience of recent investigators. The statements in the *Lancet*, Feb. 2, 1901, refer to experiments made under these conditions.

† The temperature at which the deposit of selenium from the hydrogen and hydrogen selenide current appeared was found to be 350°. When once started, the reaction proceeds even at a lower temperature through catalytic action (compare M. Bodenstein, *Zeit. Physikal. Chem.*, xxix., 429). No selenium deposit is obtained on porcelain from the flame under the above conditions.

* The estimation was made by weighing the part of the tube with the deposit obtained from 20 m.grms. selenious acid after one and a half hours, dissolving out the selenium by cyanide of potassium solution and weighing back. It is interesting to note that no difference was observed in the size of the selenium deposit when, for the generation of the hydrogen, HCl was used instead of H_2SO_4. Selenic acid and its salts, although necessitating a long time for their reduction, seemed to give rise to a slightly larger deposit in the tube.

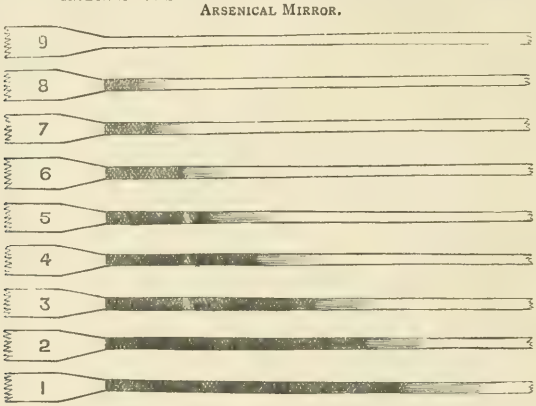
† It is possible that the non-formation of an arsenical mirror in the Manchester beers examined by Estcourt (Chemical News, 1900, lxxxii., 287, 295) was due rather to the presence of selenium than to the interference of sulphur compounds; more especially as the latter, in conjunction with arsenic, produces yellow mirrors (J. F. Smith, Chemical News, 1900, lxxxii., 315; 1901, lxxxiii., 2).

‡ Only once a sample of "pure zinc," free from sulphur, was obtained; all samples examined since contained sulphur. From 500 grms. of a certain sample of "pure zinc," which gave no reaction for arsenic in Marsh's test and was not very sensitive to arsenic, selenium was isolated in traces. Schlagdenhauffen and Pagel (*Comptes Rendus*, 1899, cxxviii., 1170) obtained a considerable deposit of selenium from 2 kilogrms. of "pure zinc." It is possible that this fact explains the different sensitiveness of various samples of zinc with regard to arsenic (see also O. Hehner, *Journ. Soc. Chem. Ind.*, xx., 195).

typical arsenical mirror.* It seems, *à priori*, probable that when selenium is in large excess of the arsenic, a red deposit would be obtained, especially if the hydrogen evolution be very rapid. Working under the above conditions, however, this was never observed, even when the quantity of selenious acid was 100 times that of arsenic.

If, for the purpose of these experiments, instead of using solutions of these substances in water, we take solutions of them in liquids containing organic and sulphur compounds (such, for instance, as beer), it will be observed that selenious acid alone (1 grain per gallon), in the absence of a lead acetate wash-bottle, produces no brick-red deposit in the tube. After one and a half hours a very faint whitish deposit of sulphur was obtained. Evidently the hydrogen selenide is reduced completely by the organic matter. In the presence of arsenic and selenious acid the arsenical mirror, in the absence of lead acetate, is usually deposited in the early stage of the experiment as described above, namely, in two portions, an anterior reddish brown and a posterior black one. If the quantity of arsenic be very small, the mirror formation is arrested at this stage. The relative

Influence of Selenious Acid on the Formation of the Arsenical Mirror.



As_4O_6. Mgrm.	H_2SeO_3. Mgrms.
1	20
1	20
1	10
1	5
1	2
1	1
1	0·5
1	0·3
1	—

(Original size).

distinctness of the brown portion is due to the formation of the solid hydrogen arsenide and to the amount of sulphur and organic compounds present, and is not dependent in any way on the presence of selenium. This can easily be shown by adding to a beer, free from arsenic, known quantities of selenious and arsenious acid, and to another sample of the same beer the same quantity of arsenic alone. Experiments were made with beer mixed with 1 grain of arsenic and 0·3 grain of selenious acid per gallon (and, in another case, one-tenth grain of arsenic and one-twentieth grain selenious acid per gallon), and absolutely identical arsenical mirrors were obtained from the arsenic beer and the arsenic+selenium beer. In both cases the mirror consisted of two portions; the one nearer to the heated part being of a brownish tint, whilst the posterior part was of a pure black colour. When the organic matter was destroyed in these two beers, they still gave identical mirrors—the brown portion, however, not being so well marked. It is evident from the above results that, when selenium is present in beer together with arsenic, no conclusion can be drawn concerning the presence or the absence of the former substance from the colour of the mirror.

Since, so far as we are aware, this anomalous behaviour of arsenic and selenium in the presence of each other has received no explanation supported by analytical facts, we thought it of interest to investigate more closely the reddish-brown deposit formed in the generating vessel. For this purpose a somewhat larger amount was prepared, filtered, and dried *in vacuo*. The product, mechanically contaminated with small particles of zinc, was partly soluble in potassium cyanide, and easily soluble in sodium hydrate. Both solutions gave a brick-red deposit of selenium upon the addition of hydrochloric acid. The solution in sodium hydrate, after the removal of the selenium from it, was found to contain arsenious acid. These facts afford an explanation of the point in question. The deposit in the generating vessel consists of a mixture of selenium and arsenium selenide (probably As_2Se_3), and its formation is evidently due to the interaction of the small quantity of hydrogen selenide (evading complete reduction to selenium), and the arsenious acid. The following equation expresses the reaction:—

$$As_4O_6+6H_2Se=2As_2Se_3+6H_2O.$$

The reaction was studied separately. Dry hydrogen selenide mixed with hydrogen (prepared by heating selenium in a dry hydrogen current), was passed through a slightly acidified arsenious acid solution. The formation of a reddish-brown deposit began at once. After filtering and drying, it was found on examination to be identical with the compound prepared and analysed by Uelsmann (*Lieb. Annalen*, vol. cxvi., p. 122), corresponding to the formula As_2Se_3.

In addition to the chemical explanation just given there are also mechanical reasons for the non-formation of hydrogen arsenide in the presence of selenium in the Marsh generating-flask. The zinc becomes completely covered with the selenium compound in question, and thus the evolution of hydrogen is prevented. If hydrogen be passed through the liquid from an outside source a small arsenical mirror is formed.

The influence of selenium on the formation of the antimony mirror was found to be analogous to that exerted on the arsenical mirror in every respect.

* The formation of two portions in the arsenical mirror is well known (compare, for instance, A. W. Blyth, "Poisons, their Effects and Detection," p. 526). J. W. Retgers (*Zeit. f. Anorg. Chem.*, 1893, 439) showed that the brown portion consists of a solid modification of hydrogen arsenide (AsH), distinguishable from the black arsenium deposit by its solubility in boiling xylol, methylene iodide, and potassium hydrate. Probably impurities of the zinc (sulphur, carbon compounds, &c.) also influence the colour of the deposit.

2. *Behaviour of Selenium in Reinsch's Test.*

It has already been pointed out by Reinsch himself that selenious acid forms a black coating on pure copper-foil, resembling that produced by arsenic (*Neues Jahrbuch. f. Pharm.*, 1866, 202). Later, Drinkwater (*Analyst*, vol. viii., p. 241), made the same observation independently, and also drew attention to its importance in toxicology. This latter observer states that the distinctly crystalline sublimate obtained from the copper does not resemble arsenic, and dissolves in sulphuric acid with a green colour.*

According to our own observations selenic acid as well (in distinction from arsenic acid), is easily reduced and precipitated on copper-foil in the presence of hydrochloric acid. This fact is explained by the previous reduction of selenic to selenious acid by boiling with hydrochloric acid alone. On long-continued boiling selenium as such is deposited, not only on the copper-foil, but in the liquid as well, producing a red colouration of the latter.

On subjecting the blackened copper-foil to sublimation in a glass tube, a small amount of a crystalline sublimate of selenium dioxide is obtained. The greater part of the selenium is retained on the foil as copper selenide. Owing to its highly hygroscopic properties it is somewhat difficult to observe the crystals under the microscope, as they immediately absorb moisture, becoming transformed into selenious acid (H_2SeO_3). If no special precautions be taken the formation of this sublimate may easily be overlooked. If the tube, containing apparently only droplets of water, be left in the desiccator over sulphuric acid for a few hours, fern shaped crystals of selenious acid are formed, and may easily be identified by micro-chemical reactions. (Reaction with iodide of potassium, reduction by zinc or stannous chloride and HCl, &c.; compare Behrens, "Microchem-Analyse"). The selenium remaining on the copper may be dissolved by means of a weak potassium cyanide solution, from which it is re-precipitated by hydrochloric acid, and may then easily be identified by the usual reactions.

By a simple modification the whole of the selenium deposited on the copper may be obtained as a sublimate. For this purpose a current of dry oxygen is passed through the tube during the sublimation, and a white ring of beautiful transparent prismatic crystals is formed. The copper-foil must be heated for some time. The same effect is obtained by a slow current of dry air, but the process must be continued for some hours. If one wishes to preserve these crystals of selenium dioxide for future observation, it is necessary to introduce some chloride of calcium, wrapped in filter-paper, into the upper part of the tube, before closing it up, sufficient moisture being present even in the closed tube to destroy the shape of the crystals.

Modification of Reinsch's Test.—If a liquid containing small amounts of selenious acid be treated in the way indicated by Reinsch, replacing, however, the copper-foil by polished silver-foil, suspended by means of a silver wire, it will be noticed that the silver quickly assumes a reddish and afterwards a bluish-black tint. No selenium is deposited in the liquid. This behaviour affords a convenient test for selenium in the presence of arsenic. The latter is under these conditions either not deposited at all, or only to an infinitesimal extent. On subjecting the dry blackened silver-foil to sublimation in a glass tube over a spirit-burner a sublimate is easily obtained, the silver reassuming its usual appearance. The sublimate consists in this case partly of selenium (producing a red tinge), and selenium dioxide. It it be desired to preserve the sublimate in its crystalline form the same precautions have to be taken as described above. Microscopically the sublimate consists of separate prismatic crystals. In that part of the sublimate in which selenium, as such, is present the crystals are arranged in fern-shaped masses. The crystals vary in length from 0·07 to 0·9 m.m., and are further characterised and distinguishable from arsenic by being doubly refractive when viewed in polarised light.

By this method a copious sublimate is obtained from 100 c.c. of a solution containing 1 : 1,000,000 selenious acid. If arsenic and selenium are present together in solution the former may be precipitated on copper-foil, after the removal of the selenium by repeated treatment with silver-foil. This method in suitable modification gives quantitative results in the absence of organic substances. Sulphur compounds blacken silver-foil, but no sublimate is obtained from it.

3. *Behaviour of Selenium in Gutzeit's Test.*

Hydrogen arsenide evolved by the action of zinc and hydrochloric acid on arsenicated material produces characteristic stains on filter-paper moistened with silver nitrate or mercuric chloride solution. Pure hydrogen selenide gives rise to similar stains. The above test, especially the silver one, is extremely sensitive when certain precautions are taken (1/1000 m.grm. being distinctly shown). The absence of hydrogen sulphide must, however, be ensured, and is best obtained by the use of acetate of lead. Under these circumstances selenium compounds have no influence on the test, being completely retained, except that when present in large quantities they keep back the arsenic as explained above under Marsh's test.

4. *Behaviour of Selenium in Bettendorf's Test.*

This test, which has been adopted by the German Pharmacopœia for the detection of arsenic in glycerin, consists in the action of stannous chloride dissolved in strong hydrochloric acid on arsenic. It has already been pointed out by Dawydow (*loc. cit.*), that selenium interferes in this test by masking the presence of arsenic. Selenium, in distinction from arsenic, is already precipitated immediately in the cold, whilst the reaction with arsenic proceeds slowly, and is only complete at higher temperatures. The drawback of this very sensitive test is that colourless solutions are necessary, and that stannous chloride is apt to contain impurities (such as sulphates, bismuth, iron, &c.), interfering with its use for the detection of arsenic (compare Dietze, *Zeit. Anal. Chem.*, 1900, 44).

Behaviour of Selenium in the Electrolytic Test.

If a solution of arsenious acid be decomposed electrolytically a part of the arsenic is deposited in the metallic state, the remainder escaping as hydrogen arsenide. In the presence of hydrochloric acid the greater part of the arsenic is transformed into the hydrogen compound, and may be identified by the usual methods (Bloxam's electrolytic test). The reaction, however, is not quantitative (Moore, CHEMICAL NEWS, liii., 209).

A few experiments showed that selenium is easily deposited as such from its solutions, acid as well as alkaline. Some hydrogen selenide, however, is produced, and subsequently partly decomposed (compare also Schucht, *Zeit. f. Anal. Chem.*, xxii., 495). The deposition of selenium from alkaline solution indicates a qualitative (and perhaps quantitative) method for its separation from arsenic, as the latter when present as arsenic acid is not electrolytically decomposed in alkaline solutions. The character of the selenium deposit (if flocculent or adhering to the platinum vessel), depends, however, very much upon the current density, temperature, &c., conditions which have not yet been worked out sufficiently to permit of this behaviour of selenium being made use of analytically.

The chief results of the above observations may be summarised as follows:—

* It may be noted here that from the green solution obtained by dissolving Se in H_2SO_4 at about 100°, selenium separates upon the addition of water as a red precipitate. On heating the solution, however, or on prolonged exposure to air, a colourless or reddish solution is produced from which no selenium is precipitated upon the addition of water. The Se is oxidised with evolution of sulphurous acid, to selenious and selenic acid, and it is probably in this state chiefly that selenium occurs in commercial sulphuric acids. (Compare Hilger, *Lieb. Ann.*, clxxi., p. 211).

1. Marsh's test gives no indication of the presence of selenium if it be accompanied by arsenic.
2. The magnitude of the arsenical mirror is influenced by the presence of selenium. Under certain conditions its formation is completely inhibited.
3. Reinsch's test, as ordinarily performed, is applicable for the detection of selenium, and can be used for its separation from arsenic if silver-foil be substituted for copper-foil.
4. None of the above methods are applicable for the quantitative estimation of small amounts of selenium together with arsenic in complex organic liquids, such as solutions of brewing sugar or beer.

Having demonstrated the presence of selenium in sugar and beer, implicated in the recent epidemic, Dr. Tunnicliffe and myself naturally turned our attention to its quantitative estimation. We therefore proceeded to work out a special method for this purpose, into which we shall enter fully elsewhere in a detailed communication on this subject.

King's College, London,
May, 1901.

A COMPARATIVE CRYSTALLOGRAPHICAL STUDY OF THE DOUBLE SELENATES OF THE SERIES $R_2M(SeO_4)_2.6H_2O$—SALTS IN WHICH M IS MAGNESIUM.*

By A. E. TUTTON, B.Sc., F.R.S.

This memoir on the magnesium group of double selenates, in which R is represented by potassium, rubidium, and cæsium, is analogous to that which was presented to the Society in March, 1900, concerning the zinc group.

The conclusions derived from the study of the morphological and physical properties of the crystals of the three salts are generally similar to those arrived at from the study of the zinc group. There is observed an uniform progression with regard to every property in accordance with the order of progression of the atomic weights of the three alkali metals present. That is to say, the constants of the rubidium salt are generally intermediate between those of the potassium and cæsium salts.

The magnesium group has, however, proved particularly interesting, inasmuch as the progressive diminution of double refraction, according to the rule which has now been established for this series of double sulphates and selenates, leads in the case of cæsium magnesium selenate to such close approximation of the three refractive indices that the crystals of this salt exhibit exceptional optical phenomena. This includes dispersion of the optic axes in crossed axial planes at the ordinary temperature, the uniaxial figure being produced for wave-length 466 in the blue; and the formation of the uniaxial figure for every wave length of light in turn as the temperature is raised, the attainment of uniaxiality for red lithium light occurring at the temperature of 94°. As the life-history of the salt terminates at 100°, owing to the presence of water of crystallisation, this substance exhibits the property of simulating uniaxial properties at some temperature within its own life-range for every wave-length of light, while still retaining the general characters of monoclinic symmetry, including slight dispersion of the median lines. In this respect it resembles to a truly remarkable extent the analogous sulphate, which the author has shown to possess like peculiarities, but it is even more striking than the sulphate, as the dispersion is much larger. It is interesting to observe that these optical properties of cæsium magnesium selenate could have been predicted, given the constants of the potassium salt, and the rules of progression established for the double sulphate, and for the zinc group of double selenates. For the double selenates resemble the double sulphates so closely that in general it may be said that their properties are precisely parallel, the constants and curves being merely moved on to a slight extent by the replacement of sulphur by selenium without disturbing their relationships.

* Abstract of a Paper read before the Royal Society, May 23rd, 1901.

THE LITERATURE OF ALCHEMY.*

By HENRY CARRINGTON BOLTON.

(Concluded from p. 270).

Another feature of certain writers on alchemy was an attempt to give a hermetic interpretation to the fables and mythology of ancient Greece and Rome; Glauber cites from an earlier author the following ingenious way of explaining the Story of the Argonautic Expedition.

"When ancient Philosophers by poetical parables described the laborious navigation of Jason to the Island Colchos where resided an huge dragon vomiting fire, which with eyes never closed diligently watched the Golden Fleece, they added this, viz.: that Jason was taught by his wife Medea to cast to this waking dragon an edible medicine to be swallowed whereby he should be killed and burst; and that Jason should presently take the dragon thus slain, and totally submerge him in the Stygian Lake.

"Jason, in this ingenious fable, hieroglyphically represents the Philosophers; Medea, accurate meditations; the laborious and perilous navigation signifies manifold chemical labours; the watching dragon vomiting fire denotes saltpeter and sulfur; and the Golden Fleece is the tincture or soul of Saturn, by the help of which Jason restored health to his aged father and acquired to himself great riches. By the pills of Medea is understood the preparation of sulfur and Sal Mirabile. By the total submersion of the dragon in the Stygian Lake is intimated the fixation of sulfur by Stygian water, *i.e.*, *aqua fortis*.

"Whence it is sufficiently clear how obscurely the ancient Philosophers did describe their fixation of sulfur by nitre, and how secretly they hid it from the eyes of the unworthy."

So far Glauber, whose discovery of the well-known medicine still called "Glauber's salts" is herein alluded to.

This association of mythology and alchemy was a favourite subject with many authors, and has been exhaustively discussed by the French Abbé Pernety in his "Mytho-Hermetic Dictionary" and in his "Egyptian and Greek Fables Unveiled." (Paris, 1758).

Plain prose has been found by a number of authors far too commonplace for recording their golden inspirations, and they have resorted to versification; this was early done by the Arabians, whose lines glow with the warmth and brilliancy of Oriental imagery. Spanish poets followed in the same vein.

Several notable poems in French have been often reprinted; one of the earliest was the "Roman de la Rose" composed by Guillaume de Loris, and extending to 1800 stanzas. In 1320 a portion of this was adapted by Jean de Clopinell, also known as Jean de Meung, whose new verses were entitled: "Les remonstrances de la nature a l'alchimiste errant." In 1413 Jean de la Fontaine, of Valenciennes, composed: "La Fontaine des amoureux de la Science." These, with others of like topics, were printed in a tiny little volume by Pierre Rigaud, at Lyons in 1618.

Their sturdy neighbours across the Channel were not long behind the lively French; among the celebrated poems of John Gower and of Chaucer were clever exposures of the chicanery of swindling alchemists, both dating from the 14th century. In 1471, Sir George Ripley, Canon of Bridlington, Yorkshire, dedicated to King Edward IV.

* From the *Pharmaceutical Review*, vol. xix., Nos. 4 and 5.

a poem of over 300 stanzas entitled: "The Twelve Gates of Alchemy"; these gates were Calcination, Solution, Separation, Conjunction, Putrefaction, Coagulation, Cibation, Sublimation, Fermentation, Exaltation, Multiplication, and Projection.

The quaint style of this poem may be observed by citing a single stanza, the last one.

> "Thus here the Tract of Alchemy doth end,
> Which Tract was by George Ripley, Canon, penn'd.
> It was composed, writ, and signed his own,
> In Anno twice seven hundred, seventy-one.
> Reader! assist him, make it thy desire,
> That after life he may have gentle fire!"

The hermetic poems written in English were collected by Elias Ashmole, the British antiquary, and printed in a volume having the title: "Theatrum Chemicum Britannicum," London, 1652. This book, which is illustrated with curious engravings, is much prized by bibliophiles. One of the fragments by an anonymous author is worth reproducing.

> "I asked Philosophy how I should
> Have of her the thing I would.
> She answered me, when I was able
> To make the water malleable:
> Or else the way, if I could find,
> To measure out a yard of wind;
> Then shalt thou have thine own desire,
> When thou canst weigh an ounce of fire.
> Unless that thou canst do these three
> Content thyself, thou get'st not me."

The Latin hexameters on the "Art of making Gold," written by Aurelius Augurelli in 1514, and dedicated by him to Pope Leo X., gave rise to an amusing incident; the Pontiff accepted the manuscript and rewarded the poverty-stricken author by the gift of an empty wallet, remarking that one who knew so well how to create the precious metal would have no difficulty in filling his purse.

The hermetic authors who produced books in the 16th to the 18th centuries, clothed their magnificent promises of immeasurable riches in very shabby attire; with few exceptions the insignificant volumes are printed with worn-out or badly cut type, on paper of poor quality, which is now stained yellow with age and damaged by careless handling. Some are injured by exposure to the acid fumes of laboratories, others are scorched by contact with furnaces, and many are disfigured by students who had the reprehensible habits of underscoring in ink lines on the printed pages, or of scribbling on the margins, thus spoiling the beauty that the books never had; moreover they were rarely bound in any material better than coarse boards or pigskin, so that alchemical literature does not appeal to lovers of works of art.

On the other hand, the unattractive looking volumes are often illustrated with curious engravings representing in strange hieroglyphics the secrets of the Philosophers' Stone; no verbal description can do these mystical pictures justice. The "Liber Mutus," as its name suggests, has no text, but fifteen plates purport to depict the mysteries of transmutation; these were drawn by Jacques Saulat Demarets and first published in 1677; they are intelligible only to the initiated.

The "Chemical Pleasure-Garden" (Viridarium Chemicum), composed by Daniel Stolz von Stolzenberg, a Bohemian physician, and printed at Frankfurt in 1624, consists of 106 emblematic plates accompanied by as many stanzas.

The earliest papyri as well as the latest products of the nineteenth century abound in arbitrary signs and characters representing substances, apparatuses, and processes, first used as a kind of shorthand; these make the books utterly unintelligible without a key. The "Alchemical Oracle," published at Ulm in 1772, contains a key to more than 2000 of these signs; some common substances had many synonymous characters, mercury was denoted by 39, alum by 26, borax by 35, distillation by 13, and a pound weight had four distinct symbols. To further mystify readers a given sign was used to designate several different articles.

The literature of alchemy reflects on its pages the intellectual environment of the pseudo-scientists producing it; the very earliest treatises show the influence of magic, astrology, and Gnosticism; then followed works in which Christian piety intrudes itself upon rhapsodies extolling the "Great Work"; somewhat later the writings exhibited a more practical phase, with attempts to adapt chemical knowledge to the healing art, which was the special honour of Paracelsus. A few decades later the literature became imbued with the fantastic tenets of theosophy, and with the transcendental vagaries of Rosicrucianism, whose advocates adopted as much of alchemical theory as suited their purposes. In proportion as the truths of scientific chemistry became known, the absurdity of the claims of the alchemists became more apparent, their writings acquired a more sober hue, and they finally made serious efforts to reconcile the two philosophies; at the close of the eighteenth century vain attempts to bolster up the sick patient were printed under the specious title "Higher Chemistry." "Higher," or esoteric chemistry, was chiefly cultivated in Germany, where appeared books with such titles as: "The Sign-Post of Alchemy" (Wegweiser, 1773), "The Pocket-Book" (Taschenbuch, 1790), and the "Magazine for Higher Natural Science and Chemistry" (1784).

Like many other superstitions, belief in alchemy took such deep root in the popular mind that it has been hard to eradicate the noxious growth, and even to-day men write and publishers print books proclaiming views quite as preposterous as those of the palmy days of the pseudo-science. It is truly extraordinary that in France, of all countries, an apparently earnest effort is being made to perpetuate the grossest follies of hermetism; there is in Paris an Alchemical Association now publishing a monthly journal advocating transmutation, hermetic medicines, and magic (L'Hyperchimie), and a "University of Higher Studies" in which Magic, the Kabbala, Occultism, and Spiritism are taught by Professors claiming for themselves esoteric knowledge of supernatural origin. A member of this unique faculty published in 1897 a text-book with the title: "How to become an Alchemist," which reads like a modernised Greco-Egyptian Papyrus.

This reference to nineteenth century books on alchemy published in France prompts brief notice of those in the English language during the same period; these are usually reprints of valued works or new translations, and their existence is probably one result of the recent revival in Astrology, Chiromancy, and Occult Science that has taken place on both sides of the Atlantic.

About fifty years ago, Ethan Allen Hitchcock, of St. Louis, wrote three works of a serious character; in "Remarks on Alchemy" (Boston, 1857), he argues that the alchemists were reformers, and he endeavours to "rescue from undeserved opprobrium the reputation of a class of extraordinary thinkers;" in "Remarks on the Sonnets of Shakespeare," Mr. Hitchcock attempts to give them hermetic significance: and the title of the third volume, "Swedenborg, an Hermetic Philosopher" (New York, 1858), explains itself.

More recently, unscrupulous men have published documents in which they claim to have found scientific processes for transmutation, and offer shares for sale in companies to exploit the same; but advertisement of dishonest enterprises do not form a legitimate part of the literature of alchemy.

During the last decade Mr. Arthur Edward Waite, in England, has shown himself to be a most industrious devotee of hermetic literature by issuing new translations of Latin works to the extent of eleven volumes, two of which are in small folio. Mr. Waite had the eccentricity to print only six copies of one of his books before distributing the type; at several guineas a copy they were taken chiefly by British libraries and collectors of rare books.

I am sometimes asked whether in my study of the writings of the alchemists I have found anything new or

of practical value to chemists; I am obliged to answer, emphatically No. The followers of Hermes made valuable contributions to the growing science of chemistry by increasing the number of acids, salts, metals, and compounds, but a false philosophy prevented them from appreciating the real significance of their discoveries; moreover, the writers chose to clothe their incoherent thoughts in a stilted, meaningless phraseology, they made wild assertions bordering on insanity, and the only redeeming feature of their sophistries was their sublime faith.

Washington, D.C.

ON THE RESULTS OF A SEARCH FOR OTHER SUGARS THAN XYLOSE AND DEXTROSE IN THE PRODUCTS OF THE HYDROLYSIS OF WOOD FROM THE TRUNKS OF TREES.*

By F. H. STORER,
Professor of Agricultural Chemistry, Harvard University.

(Continued from p. 271).

D. *Experiments on the Acid Hydrolysis of Cotton.*—In a preliminary trial a quantity of worn-out cotton cloth was boiled in several successive fresh portions of sulphuric acid of 2·8 per cent H_2SO_4, and the residual cotton left after this treatment was soaked in sulphuric acid of 86·3 per cent H_2SO_4 for twenty-four hours. Subsequently, water enough was added to reduce the acid to the strength of 2·8 per cent, and the mixture was heated during 5·5 hours on a boiling water-bath. On neutralising with calcium carbonate, evaporating to the consistence of a thick syrup, and mixing this syrup with strong alcohol, a considerable quantity of sticky, gummy matter was left undissolved.

In another trial 50 grms. of the cotton cloth were treated directly with 100 c.c. of sulphuric acid of 90 per cent H_2SO_4, and the mixture was left to stand during twenty-four hours, with occasional stirring. It was then poured into enough boiling water to reduce the acid to the strength of 6 per cent, and the boiling was maintained over a free flame for three hours. The filtered liquid was neutralised with calcium carbonate, evaporated, decolorised with bone-black, and tested with Fehling's liquor and in the polariscope. A rotation of quasi-$[\alpha]_D = 75{\cdot}88°$ was noted. The solution was evaporated to dryness, and the residue was treated with cold, strong alcohol, in which the larger part of it dissolved, the matter insoluble in alcohol being manifestly less in this case than in the preceding instance. On testing this insoluble matter after it had been taken up with water and decolorised with bone-black, a rotation of quasi-$[\alpha]_D = 81{\cdot}58°$ was noted, and "sugar" enough to amount to 0·5 per cent of the dry cloth. The matter soluble in alcohol, after having been decolorised with bone-black, gave quasi-$[\alpha]_D = 66{\cdot}62°$, and "dextrose" to the amount of 15·83 per cent of the dry cloth.

On again evaporating to dryness the solution of the matter soluble in alcohol, and treating this new residue with cold, strong alcohol, a portion of it was left undissolved, though the undissolved matter was small in proportion to that which went into solution. This matter undissolved by alcohol was taken up with water, decolorised with bone-black, and tested with Fehling's liquor and in the polariscope. Taking the sugar found as "dextrose," the rotatory power was quasi-$[\alpha]_D = 63{\cdot}66°$, while the matter that dissolved in the alcohol gave quasi-$[\alpha]_D = 63{\cdot}69°$ when similarly tested.

Subsequent trials, made after the study of birch and maple woods as above described, gave the results which here follow:—Sixty grms. of the cotton cloth were left to soak during twenty-four hours with 70 c.c. of sulphuric acid of 90 per cent of H_2SO_4, the mixture was poured into enough boiling water to reduce the acid to the strength of 3·5 per cent, and the boiling was continued during three hours over a free flame. The filtrate was neutralised with barium hydroxide, and evaporated to a syrup which was treated with successive portions of strong alcohol, as long as the alcohol became coloured. The matter insoluble in alcohol gave quasi-$[\alpha]_D = 71{\cdot}76°$.

Attempts to obtain crystals from the matter insoluble in alcohol, by operating in the manner described on page 257, failed, though an abundance of inorganic matter was encountered. After expelling alcohol, by warming upon a water-bath the matter insoluble in alcohol, a small quantity of water was added to a portion of it, the mixture was heated to a temperature somewhat higher than 50°, and set aside in an exsiccator over sulphuric acid. The mass hardened somewhat, although no crystals appeared. Another portion was tested for mucic acid by treating it with nitric acid after it had been dried for a short time at about 100°, and left over-night in an exsiccator, but the precipitate formed by the action of nitric acid was found to consist wholly of inorganic matter. When ignited on platinum foil it did not blacken, but remained white and unchanged.

In the hope or removing this inorganic contamination, a part of the matter insoluble in alcohol was dissolved in water, a current of carbonic acid was passed through the solution during several hours, and the whole was boiled thoroughly. No precipitate of barium carbonate formed, not even when these processes were repeated a second time. The solution was then evaporated, and the residue was heated to 100°, after which it was taken up with water, and treated with dilute sulphuric acid added in slight excess. The precipitate of barium sulphate that formed was removed by filtration, and lead carbonate was added to the filtrate to get rid of the sulphuric acid. After filtration the solution had an acid reaction when tested with litmus paper, but it gave no precipitate when tested with barium nitrate. Sulphuretted hydrogen gas was passed to remove lead, the filtrate from the lead sulphide was evaporated to dryness, and the residue was treated with successive portions of strong alcohol of 93 per cent. The matter insoluble in alcohol gave a slight acid reaction on being dissolved in water, and a rotation of quasi-$[\alpha]_D = 111°$. The solution was again evaporated to dryness, and tested for crystals as before (see page 257), but none appeared. The dark brown syrupy mass, on being treated with successive small portions of pure methyl alcohol, dissolved completely. This methyl alcohol solution set aside in a cold room, in mid-winter dried down to a syrup of the same appearance as before; it was now washed with ethyl alcohol of 93 per cent until all traces of acidity had been removed from it. On being dissolved in water it tasted somewhat bitter, with a suggestion of sweetness. A portion of it was tested for mucic acid, with nitric acid, and none was found—a result which coincides with that of a similar trial made by Braconnot.

Yet another portion of the matter insoluble in alcohol (see above), was dissolved in water and filtered, dilute sulphuric acid was added, to precipitate barium, if possible, and subsequently lead carbonate to remove sulphuric acid. Sulphuretted hydrogen was passed to remove lead, and, since the solution gave an acid reaction after the removal of the lead sulphide, a new quantity of lead carbonate was added, and afterwards sulphuretted hydrogen. It appeared however, that the acidity could not be annulled by this method of procedure. It was only by evaporating the filtrate from the lead sulphide to the consistence of a syrup, and washing this syrup with strong alcohol, that the last traces of free acid were removed. The syrup thus washed, when freed from alcohol and dissolved in water, had a peculiar, disagreeable odour, and a sweetish though somewhat bitter taste.

After complete removal of the acidity the syrup was dried carefully at a temperature of 70° to 80° C., and finally weighed after it had been heated for a short time to 100°. The rotatory power of this matter, based on the

* *Bulletin of the Bussey Institution*, 1900, vol. ii., Part 9.

actual weight of the solution examined, was found to be $[\alpha]_D = 63{\cdot}22°$; and on testing the solution with Fehling's liquor it appeared that the reducing power was 0·2163, that of pure dextrose being regarded as equal to 1—that is to say, the reducing power was about one-fifth that of pure dextrose anhydride. It is noteworthy that on calculating the rotatory power from the quantity of "dextrose"—that is, reducing matter—shown by Fehling's liquor to be present in a measured volume of the solution, the extraordinary figures quasi-$[\alpha]_D = 330{\cdot}9°$, were obtained.

For the sake of testing more explicitly than had been done in any of the foregoing experiments, some current statements as to the large percentage of dextrose that may be obtained on hydrolysing cotton, after treatment with strong sulphuric acid, the following trials were made:—

I. After Flechsig (*Zeit. fur Phys. Chem.*, vii., 528), 250 grms. of air-dried, well-worn cotton cloth, that had been cut into small fragments, were put, little by little, into a cooled mixture of 1250 grms. commercial sulphuric acid of 92·5 per cent H_2SO_4 and 420 grms. of water. After the lapse of one hour the mixture of cotton and acid was diluted with two-thirds its volume of water, and the whole was left to stand for one day. According to Flechsig, the mixture should now have been filtered; but it was so thick and adhesive that filtration was simply impossible. Instead, therefore, of filtering and making up the volume of the filtrate to 2·5 litres, enough water (some 700 c.c.) was added to the mixture of acid and cotton to bring its volume up to 2·5 litres, and it was found to be practicable to filter this mixture slowly with the aid of a suction pump. From the filtrate thus obtained, 50 c.c. were taken and mixed with water enough to bring the volume up to 900 c.c.; and the solution thus diluted was boiled over a free flame for six hours, in a flask with a reflux condenser, and then neutralised with a hot solution of barium hydroxide. Finally, a small quantity of barium carbonate was added to complete the neutralisation. After filtration the neutralised liquor was evaporated to the volume of 97 c.c. It gave quasi-$[\alpha]_D = 54{\cdot}64°$, and Fehling's liquor indicated dextrose enough to amount 30·26 per cent of the cotton taken (regarded as dried at 100°).

Returning now to the soft, pasty mass which remained undissolved when the mixture of strong acid and cotton was diluted with water, efforts were made to wash and collect this material in order that its weight might be subtracted from that of the cotton taken. To this end it was stirred up repeatedly with fresh portions of water, and re-filtered many times. Although it still retained an acid taste, the greyish mass was dried somewhat on a water-bath, where it turned brown and eventually black. As soon as the pasty particles had begun to ball together on stirring a new attempt was made to wash the material, but it became pasty again on the addition of water. Finally, the matter was dried at 100° in a current of air and weighed. It amounted to 27·82 per cent of the original cotton dried at 100°. From the nature of the case, the subtraction of this highly impure material from the weight of the cotton can be regarded as affording only a rough approximation to the quantity of cotton that escaped solution; but it is noteworthy that, after the subtraction of this insoluble matter, the percentage of dextrose yielded by the cotton cloth, minus the insoluble matter, amounted to no more than 41·92 per cent of the dry cotton.

A quantity of the clear neutralised filtrate, resulting from the hydrolysis of the dissolved cotton, was evaporated to dryness on a water-bath, and the residue was treated with several successive portions of cold, strong alcohol. Apparently, less than half of the residue dissolved; and, from evidence presented on previous pages, it is to be presumed that some part of this substance insoluble in alcohol must have been inorganic matter. After expelling the alcohol and dissolving in water, the matter insoluble in alcohol gave quasi-$[\alpha]_D = 55{\cdot}25°$, and Fehling's liquor indicated enough dextrose to amount to 17·38 per cent of the original cotton (dried at 100°), or to 24·07 per cent of the cotton, after subtraction of that portion of the cotton which was left undissolved by the sulphuric acid.

Although the percentage of dextrose obtained in this particular instance is very much less than the quantity reported by Flechsig in the experiment made by him, of which the trial here reported is a repetition, it is noteworthy that the rotation observed (quasi-$[\alpha]_D = 54{\cdot}64°$) is decidedly nearer that of pure dextrose than had ordinarily been detected in any of the very large number of tests made in this laboratory on products of the hydrolysis of cotton and woods of various kinds. Moreover, the rotation here exhibited by the matter insoluble in alcohol (quasi-$[\alpha]_D = 55{\cdot}25°$), is much nearer that of pure dextrose than had been observed in this laboratory in any previous instance where analogous materials were tested. But in the previous trials, the condition under which the hydrolysis of the cotton had been carried out were less closely akin to those commended by Flechsig than in the present instance, where his method of procedure was copied as closely as possible.

It would appear, therefore, that Flechsig's method of hydrolysing cotton, by means of acid of special strength, has real merit, although the conversion of cellulose to dextrose may perhaps never be so nearly complete as he was led to believe.

II. The following trial was meant at first to be in precise imitation of the work of Winterstein (*Die Landwirthschaftlichen Versuchs-Stationen*, 1892, xiv., 383), though the method finally adopted differs from his in that lead carbonate was here used to neutralise the acid product of the hydrolysis:—

0·9302 grm. of worn cotton cloth, dried at 100°, were rubbed up with 5 grms. of sulphuric acid of 92·5 per cent H_2SO_4, and allowed to stand during twelve hours. After diluting with water, the brown solution was thrown upon a tared filter, which retained nothing. The solution was made up to 200 c.c., and boiled during two hours. A sediment formed which, on being collected, washed, dried, and weighed, was found to amount to 0·043 grm. The clear filtrate was neutralised with lead carbonate. After filtration sulphuretted hydrogen gas was passed to remove any dissolved lead, and the solution was filtered and boiled to remove the excess of sulphuretted hydrogen. On being tested with Fehling's liquor sugar enough was found to amount to 52·34 per cent of the dry cotton taken, or to 54·87 per cent of that cotton, if we subtract from the weight thereof the weight of the small quantity of insoluble matter that was deposited during the hydrolysis. These last figures correspond to 49·4 per cent of the theoretically possible dextrose (111·1), which might be obtained from 100 parts of cellulose if it were practicable to change the whole of it to dextrose. The rotatory power of the solution was found to be quasi-$[\alpha]_D = 125{\cdot}2°$.

The larger part of the solution was evaporated to the consistence of syrup, which was treated with cold, strong alcohol, in which some of it dissolved; hot alcohol dissolved little more of it than cold alcohol did. The dextrin-like residue insoluble in strong alcohol was dried at 70° C. until it ceased to lose weight. There was 0·299 grm. of it, which was dissolved in 50 c.c. water. The reducing power of this solution was tested carefully with Fehling's liquor in comparison with that of a solution of pure dextrose. It appeared that while the reducing power of dextrose anhydride was 1, that of the matter insoluble in alcohol was 0·4122. In a previous trial, where the dextrin-like material had been prepared by a more circumstantial process, a reducing power of 0·2163 was observed, as has been said.

It must be observed, however, that neither of these tests of the reducing power of the "matter insoluble in alcohol" was wholly satisfactory. I am inclined to believe, indeed, that the use of lead carbonate for neutralising the acid products of hydrolysis is inadmissible. The extremely high and manifestly abnormal rotatory power of several of the "dextrins" observed after the use of the lead

carbonate make it evident that the results obtained after neutralising with this agent are not directly comparable with those got by means of barium and calcium compounds. Several chemists have called attention to the fact that by the action of one or another lead compound on sugar the rotatory power and other properties of the sugar may be changed, and it would seem that this remark must be true also of the case where lead carbonate is used for purposes of neutralisation. It was very noticeable withal in my experiments that the syrups obtained by evaporation after the use of the lead carbonate were of decidedly darker colour than those got by neutralisation with calcium carbonate or barium carbonate or hydroxide; they were, in fact, very dark, and of unpleasant, molasses-like appearance.

A satisfactory method of separating quantitatively the dextrose and "dextrins" obtained on hydrolysing cellulose from the acid and other matters with which they are admixed is still to be desired.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 16th, 1901.

Prof. EMERSON REYNOLDS, Sc.D., F.R.S., President, in the Chair.

(Concluded from p. 275).

87. "*The Condensation of Ethylphenylketone with Benzaldehyde.*" By R. D. ABELL, B.Sc.

Under the influence of a 20 per cent solution of sodium ethylate, ethylphenylketone reacts with benzaldehyde to form:—(1) 1 : 3-diphenyl-2 methyl-trimethylene glycol, colourless needles, m. p. 98—99°; (2) impure benzal-propiophenone, as a yellow oil, boiling at 210—213° (23 m.m.); (3) 1 : 3-dimethyl-1 : 3-dibenzoyl-2-phenylpropane, $C_{25}H_{24}O_2$, plates, m. p. 162—163°.

If sodium methylate be similarly employed, only the first two are obtained, whilst a solution of potassium hydroxide in aqueous alcohol gives only benzalpropiophenone, which may be more satisfactorily prepared by using hydrochloric acid gas as the condensing agent.

If the first substance (the glycol) be oxidised by means of chromic acid, methyldibenzoylmethane is produced, and this, by the action of hydrazine hydrate, gives 3 : 5-*diphenyl-4-methylpyrazol*, which melts at 222—223°.

Benzalpropiophenone readily unites with bromine to form *benzalpropiophenone dibromide*, which is obtained as a viscid green oil by adding a solution of bromine in chloroform to one of benzalpropiophenone in the same solvent. Benzalpropiophenone with phenylhydrazine gives a *hydrazone*, $C_{22}H_{20}N_2$, yellow needles, m. p. 127—128°.

As it seemed probable that for the preparation of the third substance the previous formation of benzalpropiophenone was necessary, a mixture of equimolecular quantities of benzalpropiophenone and ethylphenylketone was treated with sodium ethylate, when a compact crystalline mass was obtained which by re-crystallisation from alcohol was separated into two isomeric compounds having the formula $C_{25}H_{24}O_2$, one in the form of plates, m. p. 162—163°, identical with the 1 : 3-dimethyl-1 : 3-dibenzoyl-2-phenylpropane mentioned above, and the other as needles, m. p. 121—122°.

Sodium methylate cannot be used instead of the ethylate in this reaction.

When the isomeride, m. p. 162—163°, was heated with alcoholic ammonia, much resinous matter was formed together with a small quantity of a substance crystallising in needles, m. p. 155—156°, which from the percentage of nitrogen found may be either triphenyldimethyl dihydropyridine, $C_{25}H_{23}N$, or triphenyldimethyl pyridine, $C_{25}H_{21}N$.

This substance was also obtained by the action of hydroxylamine hydrochloride on both isomerides.

88. "*A New Method for the Determination of Hydrolytic Dissociation.*" By R. C. FARMER, B.Sc., Ph.D.

The usual method for the determination of hydrolytic dissociation by the velocity of saponification of an ester is not applicable in certain cases, particularly those in which the acid or base under investigation is difficultly soluble in water, and is precipitated during the reaction. The author has therefore devised a new method, in which the free acid or base is determined by distribution between two solvents.

An aqueous solution of the salt of a weak acid or base is shaken with a known amount of benzene or some other suitable solvent, which extracts only one of the dissociation products. From the amount extracted, the degree of hydrolysis of the salt can be calculated, the coefficient of distribution for the substance between the two solvents having been previously determined. The method was tested with a salt of hydroxyazobenzene. The values obtained at different dilutions agreed with those required by the law of dilution given by Arrhenius. The mean values found for the hydrolytic dissociation of a salt of hydroxyazobenzene at 25° were as follows:—

Dilution in litres	32	50	64	80	100
Percentage hydrolysis ..	0·91	1·09	1·24	1·32	1·60

Owing to the intense colour of the hydroxyazobenzene, the estimations had to be carried out gravimetrically. In most cases, volumetric methods could be used with advantage, both as regards rapidity and accuracy. Similar experiments with weak bases have not yet been attempted.

89. "*The Production of some New Metallic Borides.*" By S. A. TUCKER, Ph.B., and H. R. MOODY, B.S., M.A.

The authors describe the formation and properties of four new borides, those of zirconium, chromium, tungsten, and molybdenum. These compounds were prepared by bringing an intimate mixture of the metal with boron under the influence of a temperature produced by a current of from 200 to 275 ampères, and 60 to 75 volts in the electric furnace.

Combination takes place in a few minutes with the formation of compounds which are crystalline, hard, of a high specific gravity, not easily attacked by acids, and having very high melting points. The compounds thus prepared have the following formulæ:—ZrB_4, CrB, WB_2, and Mo_3B_4.

The authors were unable to produce the borides of copper and of bismuth in a like manner, and it seems therefore as if boron had no affinity for the members of the copper group, but that it combines readily with the members of the iron group.

90. "*The Action of Lead Thiocyanate on the Chlorocarbonates.* Part II. *Carboxymethyl- and Carboxyamyl-thiocarbimides and their Derivatives.*" By R. E. DORAN.

The author has already described (*Trans.*, 1896, lxix., 324), the preparation and properties of carboxyethyl-thiocarbimide and its derivatives, and this continuation of his work deals chiefly with the thiocarbamides, thioureas, and thiocarbamates obtained from its methyl and amyl homologues. No attempt was made in this case to isolate the parent substances, but the following compounds were prepared, identified, and are described in detail:—

ab-*Carboxymethylphenylthiocarbamide*,—

$CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_5$,

white needles, m. p. 158°; ab-*carboxymethylbenzylthiocarbamide*, $CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}CH_2{\cdot}C_6H_5$, needles, m. p. 134°; ab-*carboxymethyl-o-tolylthiocarbamide*, $CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_4{\cdot}CH_3$, needles, m. p. 172°; ab-*carboxymethyl-p-tolylthiocarbamide*,—

$CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_4{\cdot}CH_3$,

short prisms, m. p. 158°; ab-*carboxymethyl-α-naphthylthiocarbamide*, $CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_{10}H_7$, needles, m. p. 193°; ab-*carboxymethyl-β-naphthylthiocarbamide*, $CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_{10}H_7$, minute needles, m. p. 184°; ab-*carboxymethylmethylthiocarbamide*, $CH_3{\cdot}O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}CH_3$, needles, m. p. 146°; ab-*carboxymethylethylthiocarbamide*, $CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_2H_5$, needles, m. p. 86°; ab-*carboxymethylisobutylthiocarbamide*, $CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_4H_9$, long prisms, m. p. 83°; *carboxymethylthiourea*, $CH_3O{\cdot}CO{\cdot}N{:}C(NH_2)SH$, short prisms, m. p. 166°; *carboxymethylpiperidylthiourea*, $CH_3O{\cdot}CO{\cdot}N{:}C(SH){\cdot}N{:}C_5H_{10}$, needles, m. p. 97°; *carboxymethylphenylsemithiocarbazide*, $CH_3O{\cdot}CO{\cdot}NH{\cdot}C(SH){:}N{\cdot}NH{\cdot}C_6H_5$, glistening plates, m. p. 180°; *methyl carboxymethylthiocarbamate*, $CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}OCH_3$, feathery needles, m. p. 45°; *ethyl carboxymethylthiocarbamate*, $CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}OC_2H_5$, needles, m. p. 83°; *benzyl carboxymethylthiocarbamate*, $CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}OCH_2{\cdot}C_6H_5$, cream-white needles, m. p. 103°.

Derivatives of carboxyamylthiocarbamide:—

ab-*Carboxyamylphenylthiocarbamide*,—

$$C_5H_{11}O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_5,$$

white needles, m. p. 97—98°; ab-*carboxyamyl-o-tolylthiocarbamide*, $C_5H_{11}O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_4{\cdot}CH_3$, white needles, m. p. 96—97°.

Carboxyamylthiourea was also obtained, but in too small a quantity to permit of its satisfactory identification.

91. "*The Chlorine Derivatives of Pyridine.* Part VII. *Some Condensation Products.*" By W. J. Sell, M.A., F.R.S., and F. W. Dootson, M.A.

A series of experiments having for their object the determination of the orientation of a compound, $C_{10}HCl_{11}N_2$, which has been obtained by the action of chlorine on pyridine hydrochloride, together with certain of its derivatives (*Trans.*, 1899, lxxv., 980) was described.

This substance, which is the principal product of the chlorination, may be crystallised unaltered from chloroform or acetone, but if the solvent contains the hydroxyl group the compound is decomposed. With benzoic and other acids it reacts, giving a theoretical yield of the acid chloride in accordance with the equation—

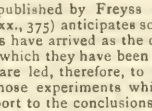
$$C_{10}HCl_{11}N_2 + C_6H_5CO_2H = C_6H_5COCl + C_{10}HCl_9N_2O + HCl.$$

The accompanying formulæ exhibit the relationship between the parent compound and certain of its derivatives.

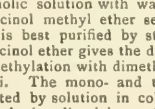
92. "*The Diazotisation of Dinitroanisidine and the Constitution of the Resulting Product.*" By R. Meldola, F.R.S., and J. V. Eyre.

A paper just published by Freyss (*Bull. Soc. Ind. de Mulhouse*, 1901, lxx., 375) anticipates some conclusions at which the authors have arrived as the outcome of an investigation upon which they have been engaged since last October. They are led, therefore, to place upon record the results of those experiments which appear to give independent support to the conclusions of the author just named. This work is an extension of that already published (Meldola and Wechsler, *Trans.*, 1900, lxxvii., 1172; *Proc.*, 1898, xiv., 226).

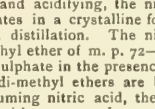
The crystalline diazo-compound, obtained by the action of a nitrite on dinitroanisidine in acetic acid solution, is a diazoxide of the formula—



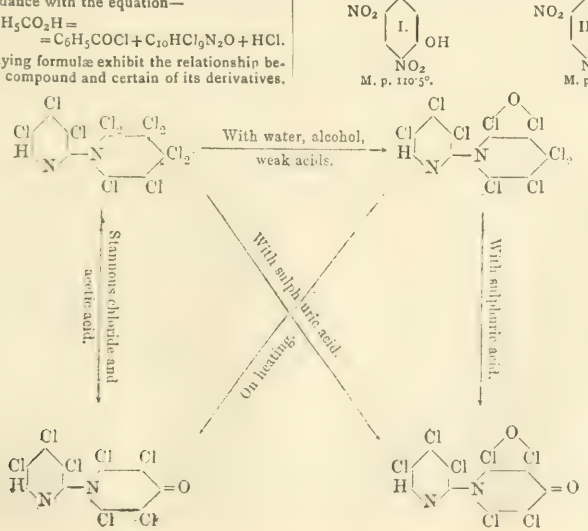
The proof of this constitution is given by several considerations, some of which appear from the experiments of Freyss, the most cogent, perhaps, being its ready convertibility into nitromethylresorcinol, $C_6H_3{\cdot}NO_2{\cdot}OH{\cdot}OCH_3 = 1:2:4$. The authors find the most convenient method for bringing about this conversion is to dissolve the diazoxide in alcoholic sodium hydroxide. The decomposition takes place at the ordinary temperature, with the evolution of nitrogen and the formation of aldehyde. On diluting the alkaline alcoholic solution with water and acidifying, the nitroresorcinol methyl ether separates in a crystalline form, and is best purified by steam distillation. The nitroresorcinol ether gives the dimethyl ether of m. p. 72—73° on methylation with dimethyl sulphate in the presence of alkali. The mono- and the di-methyl ethers are both nitrated by solution in cold fuming nitric acid, the dimethyl ether dissolving at first with a green colour. The corresponding dinitro-derivatives have the constitutions:—



M. p. 110·5°.



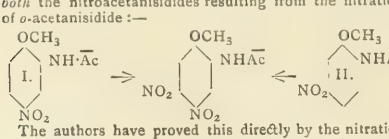
M. p. 154°.



The first of these crystallises from alcohol in large yellow plates. The second crystallises in small white needles from alcohol, and in very minute needles from boiling water; it is obtained also (mixed with colouring matters) by the direct nitration of resorcinol dimethyl ether in acetic acid with excess of fuming nitric acid, and its constitution as a derivative of resorcinol is thus confirmed. The nitroresorcinol monomethyl ether benzoylates very readily by the Schotten Baumann method. The benzoyl derivative, $C_6H_3{\cdot}NO_2{\cdot}OC_7H_5O{\cdot}OCH_3 = 1:2:4$, crystallises from alcohol in flat white needles melting at 95°. The nitro-derivative, when dissolved in acetic acid, gives an intense blue colour on the addition of zinc dust. If reduced with zinc dust and acetic acid in the presence of acetic anhydride, the acetamino-derivative, $C_6H_3{\cdot}NHAc{\cdot}OH{\cdot}OCH_3 = 1:2:4$, is obtained. This crystallises from water in lustrous flat white needles, which become brown on exposure to the air. The melting-point is 164—165°.

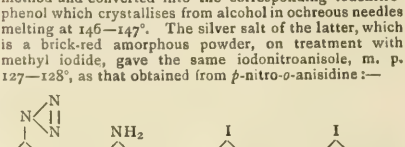
The diazoxide is remarkably stable towards acids; it can be boiled with dilute hydrochloric or sulphuric acid and can be crystallised from boiling glacial acetic acid or from acetic anhydride without undergoing decomposition. It is decomposed on boiling with hydriodic acid solution, and the product is iodonitroresorcinol methyl ether (Meldola and Wechsler, *loc. cit.*, 1173), $C_6H_2{\cdot}OCH_3{\cdot}OH{\cdot}NO_2{\cdot}I = 1:3:4:6$. The azo-β-naphthol derivative described in the former note (*loc. cit.*) has the formula $C_6H_4{\cdot}NO_2{\cdot}OCH_3{\cdot}OH{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$. In addition to the properties already assigned to this compound, it may be added that it is distinctly phenolic in character, dissolving in cold aqueous alkali with a dull claret-red colour and being precipitated unchanged by acids. The phenolic character is due to the hydroxyl group in the para-position. An examination of the product of the action of ammonium sulphide on the azo-compound has shown that no aminoazo-compound is formed, and this is in accordance with the view that the nitro-group is not in the para-position with respect to the azo-group (Meldola, *Trans.*, 1883, xliii., 425).

The constitution of dinitroanisidine (m. p. 188°) first described (Meldola and Wechsler, *loc. cit.*) follows from the fact that it is obtainable by the further nitration of *both* the nitroacetanisidides resulting from the nitration of *o*-acetanisidide:—



The authors have proved this directly by the nitration of carefully purified specimens of the mononitroacetyl derivatives. No. I. was prepared by the reduction of dinitroanisole and acetylation of the nitroanisidine (Meldola, Woolcott, and Wray, *Trans.*, 1896, lxix., 1330). No. II was prepared from the corresponding nitroanisidine, the latter being obtained pure, by a modification of the method formerly described (*Proc.*, 1898, xiv., 226). The mixture of nitroacetyl derivatives resulting from the nitration of *o*-acetanisidide is boiled with dilute alkali till completely hydrolysed. The mixed nitroanisidines on being dissolved in hot dilute sulphuric acid deposit, on cooling, silvery scales of the sulphate of the *p*-nitro-compound, $C_6H_3{\cdot}NO_2{\cdot}NH_2{\cdot}OCH_3 = 1:4:5$, the sulphate of the isomeric compound remaining in solution. The crystalline sulphate gives pure *p*-nitro-*o*-anisidine on treatment with dilute alkali and crystallisation of the product from hot water. In order to characterise further the two nitroanisidines and the dinitroanisidine, the benzoyl derivatives have been prepared:—$C_6H_3{\cdot}NO_2{\cdot}NH(C_7H_5O){\cdot}OCH_3 = 1:4:5$, white silky needles from alcohol, m. p. 149—150°; $C_6H_3{\cdot}NO_2{\cdot}NH(C_7H_5O){\cdot}OCH_3 = 1:3:4$, slender ochreous needles from alcohol, m. p. 160—161°; $C_6H_2{\cdot}(NO_2)_2{\cdot}NH(C_7H_5O){\cdot}OCH_3 = 1:2:5:4$, ochreous scales from acetic acid, m. p. 185—186°.

The constitution of the *p*-nitro-*o*-anisidine was proved by two methods differing from those adopted by Freyss, as well as by conversion into the *p*-nitro-guaiacol of m. p. 104°. The latter compound, of which the discovery is assigned to Rupe (*Ber.*, 1897, xxx., 2446), was first described by one of the authors (Meldola, *Proc.*, 1896, xii., p. 125). The *p*-nitro-*o*-anisidine when diazotised and the amino-group replaced by iodine in the usual way, gave an iodonitroanisole which crystallised in straw-coloured needles melting at 127—128°. The constitution of this compound might have been expected to correspond with that of the nitro-aminophenol, m. p. 201—202°, obtained by Friedländer and Zeitlin (*Ber.*, 1894, xxvii., 196) by heating *p*-nitrobenzenediazimide with sulphuric acid. Some of the nitroaminophenol was prepared by this method and converted into the corresponding iodonitrophenol which crystallises from alcohol in ochreous needles melting at 146—147°. The silver salt of the latter, which is a brick-red amorphous powder, on treatment with methyl iodide, gave the same iodonitroanisole, m. p. 127—128°, as that obtained from *p*-nitro-*o*-anisidine:—



The other method consisted in combining the diazotised nitroanisidine with β-naphthol in the usual way and reducing the nitroazo-compound to an aminoazo-compound by ammonium sulphide. The nitroazo-compound is obtained as a scarlet precipitate on mixing solutions of the diazonium salt and β-naphthol dissolved in sodium hydroxide. It crystallises from glacial acetic acid, in which it dissolves with difficulty, in filamentous needles of a dull red colour with a slight metallic reflex. Its melting-point is 269°. It dissolves in alcoholic soda with a violet colour and with a similar colour in strong sulphuric acid, the latter solution becoming redder on dilution with water. The solution in alcoholic soda becomes red on heating with ammonium sulphide, and on dilution with water the aminoazo-compound, $NH_2{\cdot}C_6H_3{\cdot}OCH_3{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$, separates out in bronzy scales. The melting-point of this compound is above 300°. It dissolves in alcohol with a Bordeaux-red colour, which becomes orange on adding hydrochloric acid. It dissolves in hot aqueous hydrochloric acid with a dull red and in strong sulphuric acid with a magenta-red colour, becoming more orange on dilution. The reducibility of the nitro-group without the separation of the nitrogen atoms of the azo-group may be taken as proof that the two groups are in the para-position with respect to one another.

The constitution of the nitroanisidine of Cahours (Meldola, Woolcott, and Wray, *loc. cit.*) was further proved by converting it into the corresponding iodonitroanisole by replacing the amino-group by iodine by the diazo-method. The iodonitroanisole, $C_6H_3{\cdot}NO_2{\cdot}I{\cdot}OCH_3 = 1:3:4$, melts at 95—96°, and is identical with that described by Reverdin (*Ber.*, 1896, xxix., 998).

Experiments were in progress to obtain direct evidence of the constitution of the dinitroanisidine at the time of appearance of the paper by Freyss. The triaminoanisole obtained by reducing the dinitroanisidine with tin and hydrochloric acid forms a crystalline hydrochloride, but it is very unstable, passing readily into a deep violet colouring-matter on exposure to the air. The dinitroacetanisidide does not give an anhydro-base on reduction, an observation which is in harmony with the view that the acetamino-group is not in the ortho-position with respect to a nitro-group. On the other hand, that the triaminoanisole contains two amino-groups in the ortho-position is proved by the formation of an azine with phenanthrene-

quinone. On heating together equimolecular weights of the triamine and the quinone in glacial acetic acid, the aminoazine is gradually formed, and on adding hydrochloric acid the hydrochloride is completely thrown out on cooling as a dull red precipitate. The free base is an ochreous powder which dissolves in alcohol with a magnificent green fluorescence. It does not readily crystallise, but separates from boiling toluene in the form of brown nodules having a melting-point of about 237°, but softening before this temperature. The base thus obtained contains one molecule of toluene and has the formulæ—

$$CH_3O\cdot NH_2\cdot C_6H_2\begin{cases}N\cdot C\cdot C_5H_4\\ |\quad |\\ N\cdot C_6H_4\end{cases} + C_7H_8.$$

The result of this investigation thus confirms the conclusion that on diazotising 3 : 4-dinitro-*o*-anisidine in acetic acid, it is the 4-nitro-group which is eliminated, probably in accordance with the scheme :—

$$CH_3O\cdot NO_2\cdot C_6H_2<\begin{matrix}N_2\cdot O\cdot H\\ NO_2\end{matrix} =$$

$$= CH_3O\cdot NO_2\cdot C_6H_2\begin{cases}N_2\\ |\\ O\end{cases} + HNO_2.$$

The more exact nature of the mechanism of the change will be made the subject of further investigation.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxii., No. 20, May 20, 1901.

Researches on the amount of Aluminium present in Vegetable Earths.—Th. Schloesing.—The greater number of specimens of earths from Madagascar which the author carefully examined in the course of his research, contain, often in considerable quantity, free alumina. This metal is also present as the silicate; the latter being very easily acted upon by a dilute solution of soda. The alumina and the silicate are present for the most part in a sandy condition, and do not form the agents of tenacity in the earths. Finally, the author finds that their presence appears to present no obstacle to vegetation.

Lowering of the Temperature of Maximum Density of Water produced by the Solution of Chlorides, Bromides, and Iodides of Potassium, Sodium, Rubidium, Lithium, and Ammonium; Ratio of these Lowerings amongst themselves.—L. C. de Coppet.—As in the case of the salts already examined, the lowering of the temperature of maximum density of water is proportional to the quantity of the substance dissolved. The molecular lowering is almost constant, the differences observed being attributable to experimental errors. The lithium salts, however, form an exception; their molecular lowering increases with the concentration of the solution, and this lowering is more accentuated for having been attributed to experimental errors. The author gives a table of the results obtained.

Alcohols and Carbide of Calcium.—Pierre Lefebvre.—In a previous paper, the author gave an account of the results obtained by passing the vapour of amyl chloride over calcium carbide heated to redness. This investigation is correlative to that which he now undertakes on the decomposition of the alcohols when passed over calcium carbide at a temperature of 500°. He examines the composition of the gases obtained when amyl alcohol, isobutylic alcohol, ethyl alcohol, and methyl alcohol are used. The gases in all cases consist of acetylene, ethylene, carbonic oxide, ethylenic carbides, ethane, hydrogen, and carbonic anhydride in varying proportions.

Condensation of the True Acetylenic Carbides with Formic Aldehyde. Synthesis of Primary Acetylenic Alcohols.—Ch. Moureu and H. Desmots.—By the condensation of the true acetylenic carbides, R—C≡CH, with formic aldehyde, CH_2O, the authors deduce a very simple method of synthesis of the primary acetylenic alcohols, R—C≡C—CH_2OH. After a number of fruitless attempts with an ordinary solution of formol and carbides in a free state in presence of various condensation agents, they were led to try to effect a reaction between the sodium carbides and the solid polymer, $(CH_2O)_n$, known under the name of trioxymethylene. The experiment succeeded excellently.

Action of Acid Chlorides on the Ether-oxides in presence of Zinc.—P. Freundler.—M. Freund has shown that when zinc acts on a solution of butyryl in ethyl oxide, a mixture of ethyl butyrate, ethyl chloride, and a compound corresponding to the formula of dibutyryl is produced, whilst, at the same time, zinc chloride is formed as a by-product. The action can be represented by the equation—

$$4C_3H_7.COCl + Zn + 2(C_2H_5)_2O = 2C_3H_7.CO_2C_2H_5 + 2C_2H_5Cl + ZnCl_2 + C_3H_7.CO.CO.C_3H_7.$$

The author's research confirms these conclusions. He acts with the zinc-copper couple on the chlorides of the acids, and finds his results coincident with the above, at least in so far as the formation of the ether salt and alcoholic chloride is concerned.

Oxidation of the Primary Alcohols by the Action of Contact.—J. A. Trillat.—The author's experiments show—(1) That all the primary alcohols of the fatty series are oxidisable under the influence of the platinum spiral; (2) that the oxidation of the aldehyde corresponding to the alcohol can be limited; (3) that the presence of water is not an obstacle to oxidation, but rather favours it; (4) that porous bodies and platinum black, under the experimental conditions employed by the author, give by oxidation the corresponding acids rather than the aldehydes; (5) the formation of the acetals under catalytic influence is constant at least for the first terms of the fatty series, besides which the action is reversible.

The Substitution of Zinc-white for White-lead in Oil-paints.—Ach. Livache.—Ever since 1782, efforts have been made to effect a substitution of zinc-white for white-lead in oil paints; these have in all cases proved unsuccessful. The author undertakes a methodical study of the subject. He obtained the various products employed in oil-painting, both with the base zinc oxide and the base white-lead; then, taking these as types, he examined the causes which render zinc-white inferior to white-lead. These causes once determined, he established formulæ which, if zinc-white is employed by the painter, would give results identical with the products obtained when white-lead is used as a base.

MISCELLANEOUS.

Decomposition of Albumenoids or Protoplasmides.—A. Etard.—The author finds that decalcified bones can be separated by simple hydrolysis into three groups of substances :—(1) Glycocoll, leucine, and a little tyrosine; (2) a syrupy substance which is very soluble in concentrated methyl alcohol; (3) a substance which is quite insoluble in concentrated methyl alcohol. A study of the two latter groups proves that bodies derived from albumenoids or protoplasmides should be considered as nitrated saccharides, a simple example of these being chitosamine.—*Comptes Rendus*, cxxxii., No. 19.

Elimination of a "Sulpho" Group by means of Reducing Agents.—F. J. Moore. (Preliminary notice).—The author having obtained some *p*-sulphocinnamic acid, tried, by treating it with sodium amalgam, to prepare the hitherto unknown *p*-sulphohydrocinnamic acid, but he

obtained in its place hydrocinnamic acid which can be prepared much more easily with aluminium amalgam. For this purpose the sulphocinnamic acid is dissolved in 20 parts of water, and then aluminium filings impregnated with a solution of sublimate are added; this solution, which must be made alkaline, is left all night in a warm place, and then neutralised with HCl or H_2SO_4, and extracted with ether. The hydrocinnamic acid thus extracted crystallises in warm water in long, silky neeedles, fusible at 48°. If the experiment is interrupted after two or three hours there is no hydrocinnamic acid formed, but only cinnamic acid. The reaction probably takes place in two phases according to the equations:—

$$NaSO_3.C_6H_4.CH{=}CH.COONa+H_2=$$
$$=NaHSO_3+C_6H_5.CH{:}CH.COONa;$$

$$C_6H_5.CH{:}CH.COONa+H_2=C_6H_5.CH_2.CH_2COONa.$$

The elimination of the "sulpho" group from the benzenic radicle takes place, therefore, before hydrogenation. Qualitative experiments undertaken with the object of eliminating the sulpho group of benzene-sulphonic acid, or other sulphonic acids, by means of aluminium amalgam, were unsuccessful.—*Berichte*, vol. xxxiii., p. 2014.

Direct Nitration of the Primary Aromatic Amines.—E. Tauber and F. Walder.—During some work done on Bismarck-brown the authors found that *m*-phenylenediamine could be nitrated directly in spite of its two "amino" groups, giving a hitherto unknown mononitroso-*m*-phenylenediamine. The following is the method of procedure:—324 grms. of *m*-phenylenediamine are dissolved in 2·5 litres of water and 444 grms. of hydrochloric acid; 3 kilogrms. of ice are also added. When the temperature has fallen to 0°, a cold solution of 156 grms. of nitrite of soda in 600 c.c. of water is suddenly added all at once, and stirred vigorously for at least five minutes. After standing for a few hours the product of the reaction is brought to 50°, and the Bismarck-brown formed is precipitated with 800 grms. of sea-salt; this is filtered at 30°, and washed with 1 litre of salt water at 10 per cent. The filtrate is covered over with 3 litres of ether, after which 800 grms. of powdered soda crystals are gradually added; after a few hours the nitrated base is deposited in crystals at the zone of separation of the two liquids; then, after a further twelve hours, during which time the mass is frequently stirred, the crystals are filtered off, and washed with ether; the pure substance is obtained by crystallising it in 20 parts of boiling water. Nitroso-*m*-phenylenediamine occurs in the form of brilliant brownish-red flakes or needles belonging to the monoclinic system. It is easily soluble in ether and benzene, almost insoluble in cold water, and fuses at 210°. Its hydrochlorate occurs in long reddish-brown needles, or in brilliant, almost black, prisms. The authors intend to prepare derivatives of this nitrated base, and to examine the direct nitration of other amines.—*Berichte*, xxxiii., p. 2116.

MEETINGS FOR THE WEEK.

WEDNESDAY, 19th.—Institution of Mining and Metallurgy, 8. "Sulphide Ore Treatment (Phœnix Process)," by Edgar A. Ashcroft. "Mineral Features of Pahang, Malay Peninsula," by F. J. Stephens. Notes on Winding and Pumping Plant driven by an Oil Engine," by Ll. Parker. "Additional Notes on Mine Surveying'" by G. A. Troye. "Mining and Other Statistics of the Thirty Mexican States," by A. Cairn Hodge.

—— Microscopical, 8. "An Examination of the Abbe Diffraction Theory of the Microscope," by J. W. Gordon.

THURSDAY, 20th.—Chemical, 8. Ballot for the Election of Fellows. "The Direct Union of Carbon and Hydrogen" (Part II.), by W. A. Bone and D. S. Jerdan. "Ammonium and other Imidosulphites," by E. Divers and M. Ogawa. "Nitrilosulphates," by E. Divers and T. Haga. "The Decomposition of Hydrocarbons at High Temperatures," by W. A. Bone and D. S. Jerdan. "The Sugars from Cellulose," by H. J. H. Fenton. "On a Theory of Chemical Combination," by G. Martin. "On the Occurrence of Paraffins in the Leaf of Tobacco," by T. E. Thorpe, C.B., F.R.S., and John Holmes. "Studies in the Camphane Series" (Part IV.), by M. O. Forster. "On the Decomposition of Carbon Dioxide when submitted to Electric Discharge at Low Pressures," by J. N. Collie, Ph.D., F.R.S. "Two New Substances in Lemon Oil," by H. E. Burgess.

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PHYSICS .. .. A. GRIFFITHS, D.Sc.
METALLURGY.. G. PATCHIN, A.R.S.M.

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THE CHEMICAL NEWS.

Vol. LXXXIII., No. 2169.

ON AN EXPLANATION OF THERMAL CENTRES OF STABILITY IN COMPOUNDS.

By GEOFFREY MARTIN.

In a paper "On the Existence of Thermal Centres of Stability" (Chemical News, 1900, lxxxi., 301), I gave six instances of bodies capable of existing at moderate and at very high temperatures, but incapable of existing at intermediate temperatures. To this list must now be added the case of nitrogen peroxide, which, although completely dissociated at moderate temperatures, seems to be able to exist at very high temperatures (*Nature*, May 16th, 1901, vol. lxiv., p. 67).

The following will, I think, give an intelligible explanation of the phenomenon :—

Let us imagine, as is now very probable, that an atom is not the hard indivisible unit of Dalton, but rather a very complicated system of particles in perpetual motion, and has a mobile constitution. Now the mere fact of bringing atoms into contact with each other does not necessarily lead to chemical action. Something more is required. This is well emphasised by Baker's recent experiments on the influence of impurity on chemical change. The necessary condition appears to be an "opening up" of the complex atoms so as to set free the internal forces—a process otherwise known as ionisation. A chemical atom is therefore analogous to a closed ring compound in organic chemistry. They can aggregate together by mutual attraction, but, before they can chemically combine, the atomic ring must be broken, so that the lines of force which before were contained in the circuit of the atom can now radiate into space. The atoms can then, and then only, unite chemically with other atoms. The greater the ease with which the ring opens out the more chemically active is the element concerned.

Consider, now, a gaseous system of molecules contained in a closed vessel. Each of the atoms composing the molecule has a certain internal time rate of vibration. As previously explained, these atoms are composed of particles grouped into a closed ring like that of a benzene nucleus, and are chemically inactive until the ring is broken, when the atoms become ionised. The ring may be ruptured by setting one or more of the particles composing it into such rapid oscillatory motion as to sever its connection with neighbouring particles. This may be effected if periodic impulses act on the particle, their frequency being either equal to its natural time rate of vibration or some multiple of it.

Now, as a given molecule flies through space, there is a continual flux of other molecules past it in every direction. These fluxing molecules will cause a continual variation in the intensity of the force acting on a given molecule—the ether strain increasing with the approach of a molecule and diminishing as it recedes. If many such molecules approach and recede in each second, the variations in ether strain will succeed each other with enormous rapidity. Suppose, now, this rate of variation of ether strain approaches in numerical value the natural time rate of vibration of some one particle of those composing the atomic ring, this particle will be set vibrating by a process analogous to resonance, and the rapid oscillatory motion thus produced may become so violent as to cause it to sever its connection with neighbouring particles. The ring will thus be ruptured, and the atoms will become "ionised," and therefore will react chemically on other atoms. No chemical reaction can take place until the atoms of the reacting molecules are thus ionised. Chemical combination will continue until the rate of variation of the ether strain no longer corresponds to the rate or rates of vibration of the atoms.

The bodies concerned will cease to act chemically on each other when this occurs.

But suppose now the temperature to be greatly increased, then a point will be reached when the rate of variation of ether strain will again correspond to twice, thrice, &c., the rate of vibration of the atom, and in this case again the atom will be so internally disturbed as to open out and allow chemical combination to take place once more. This then explains the recurrent nature of chemical action as instanced in the examples given in my former paper. It also explains phenomena like the phosphoresence of phosphorus which is dependent upon the narrow limits of temperature and pressure, for it is obvious that the rate of variation of ether strain due to rapidly passing atoms will vary with the temperature and pressure.

Merchant Venturers' College, Bristol,
May 25th, 1901.

A BIBLIOGRAPHY OF STEEL WORKS ANALYSIS.

Part IX.

By HARRY BREARLEY.

(Continued from p. 172).

PHOSPHORUS.

An enormous number of papers have been written on the estimation of phosphorus. Those relating exclusively to the analysis of agricultural material, except when dealing with the chemistry of the process, are not noticed. Amongst the papers dealing with metallurgical materials, there is so much repetition that a selection of those presenting new features, and a grouping together of papers on similar lines, was necessary in order to make this section of the compilation usable. The classification is :—

I. Separations from other Elements.
II. Gravimetric Estimations.
  a. Precipitating Finally with Mo.
  b. Precipitating Finally with Mg.
  c. Precipitating Finally in Various Ways.
III. Volumetric Estimations.
  a. Of the Molybdate Precipitate.
  b. In Various Ways.
IV. Miscellaneous.

I. Separations from other Elements.

Iron and Aluminium.—

1195. Schulze (*C. N.*, i., 49).—Add Sb_2Cl_3 to neutralised solution, boil the precipitate with NaHO, filter off Sb, &c., and precipitate P in the filtrate with Mg.

1196. Girard (*C. N.*, v., 281; vi., 99) and Antony and Mondolfo (*J. C. S.*, lxxvi., ii., 330).—Dissolve in HNO_3 along with Sn, dissolve SnO_2 in aqua regia, add Am_2S to precipitate traces of Fe, &c., and add Mg to the filtrate.

1197. Kessler (*C. N.*, xxiii., 76).—Dissolve Fe in HNO_3, evaporate, reduce with H_2S, precipitate with ferrocyanide, and add Mg to the filtrate. Mohr (*J. C. S.*, lii., 864).—Similarly. Titrate P with uranium solution.

1198. Chancel (*C. N.*, i., 72).—Precipitate from nitric solution with $AgNO_3$ and Ag_2CO_3; collect Ag_3PO_4, remove Ag as chloride, and precipitate P with Mg.

1199 Lyte (*C. N.*, iii., 131).—Pass H_2S to form FeO, and remove As, &c.; add $K\bar{A}$ and $Pb\bar{A}_2$, decompose

precipitate with Am_2S, and P from filtrate with Mg. Specially suited to separating P from Al and Cr.

1200. Mayer (*C. N.*, iv., 75).—Requisite proportions of reagents when P is precipitated from tartrate solutions in order to keep up tartrate of magnesia.

1201. Warington (*C. N.*, viii., 19).—Citric acid does not form insoluble Mg salts when used for holding up Fe and Al in AmHO solutions.

1202. Flight (*C. N.*, xxxi., 214).—Boil with hyposulphite. Fe and P in filtrate separated with Am_2S. Al and P in precipitate separated with NaHO and $BaCl_2$.

1203. Derome (*C. N.*, xl., 292).—Ignite with an excess Na_2SO_4, and precipitate Na_3PO_4, extracted with water, with Ur, Ag, or Mg.

Lime.—

1204. Smith (*C. N.*, vii., 212).—In the presence of tartaric acid, CaO can be precipitated as oxalate quite free from P.

1205. Williams (*C. N.*, xxi., 170).—As 1196; but dissolves the Sn-P compound in KHO, adds H_2S, &c.

1206. *SiO_2 and WO_3.*—Skey (*C. N.*, xvi., 187).—Both SiO_2 and WO_3 form insoluble compounds with P_2O_5, and on this account P estimations are frequently imperfect.

1207. *Vanadium.*—Holverscheit (*J. C. S.*, lviii., 1343).—Add SO_2 to form V_2O_4, expel excess, and precipitate P rapidly with Mo at 60° C.

1208. *Uranium.*—Reichardt (*C. N.*, xxviii., 315).—Dissolve in Na_2CO_3 and precipitate P with Mg.

1209. *Selenium.*—Same process as 942.

II. Gravimetric Estimations.

a. Precipitating Finally with Mo.—

1210. Eggertz (*C. N.*, ii., 227).—Precipitates from HNO_3-HCl solution of iron. The precipitate more soluble in 1 per cent HNO_3 than in water; tartaric acid prevents the precipitation (see 1279).

1211. Fresenius (*C. N.*, xii., 73).—The PMo* is not interfered with by HNO_3, H_2SO_4, Fe_2Cl_6, or Al_2Cl_6; it is by large amounts of HCl, AmCl, or dilution. The mixture is kept at 65° for six hours.

1212. Parry (*C. N.*, xxv., 229).—To solution of the metal add AmHO to complete precipitation, re-dissolve in HNO_3, and boil with a neutral solution of Am_2MoO_4.

1213. Holtoff (*C. N.*, xxxvi., 234).—PMo may be formed in the presence of HCl, but the temperature must be kept low. The precipitate is soluble in aqua regia, and MoO_3 is precipitated. The magnesia precipitate may contain Mo. The acetate-magnesia process gives low results.

1214. Deane (*C. N.*, liv., 174).—Usual process. The precipitate has a tendency to pass the filter when formed in very acid (nitric) solutions.

1215. Eggertz (*C. N.*, xlii., 87).—Deals with criticisms *re* the formation of the precipitate, its composition, reagents, estimation, and comparison with the Mo-Mg process.

1216. Hundeshagen (*C. N.*, lx., 169, 177, &c.).—The yellow precipitate is always $(NH_4)_3PO_4.12MoO_3$ when dried at 130—150° C. The influence of alkaline nitrates, concentration, temperature, and acidity. The formation of PMo from neutral solutions with HNO_3. The dissociation of PMo with HNO_3, and the limiting molecular proportions of its constituents for quantitative estimations. The solubility of PMo in various salts, acid, and water. P_2O_5 or MoO_3, may be estimated by titrating one against the other. Volumetric processes depending—(1) on the saturation of PMo with NaHO, and (2) on precipitating with HNO_3 from neutral solutions are outlined.

* Used throughout as a contraction for ammonium phosphomolybdate.

1217. Carnot (*C. N.*, lxvii., 101).—Preliminaries like 1241; but the PMo is dissolved and re-precipitated under well-defined conditions.

1218. Hanamann (*J. S. C. I.*, 1895, 598).—The P is precipitated and filtered at ordinary temperatures in order to assure a constant composition. Wash from the paper and ignite as 1239.

1219. Parry and Morgan (*C. N.*, lxvii., 161).—Dissolve in aqua regia and eliminate HCl. Any excess of nitric acid is corrected by AmHO after* the Am_2MoO_4 has been added.

1220. Villiers and Borg (*C. N.*, lxvii., 313).—The precipitation should be effected below 15°. In the presence of Fe and Al, a pure precipitate is not obtained.

1221. Johnson (*C. N.*, lxx., 157).—Above 50° the PMo is contaminated with Fe, Al, and Mn. The citrate method gives good results only by compensatory errors.

1222. Tauber (*J. I. S. I.*, 1883, 313).—The influence of $AmNO_3$. Mo in the $Mg_2P_2O_7$ precipitate can be eliminated at high temperatures.

1223. Huss (*J. C. S.*, I., 1073).—AmCl added to the $Fe_2(NO_3)_3$ solution in order to form Fe_2Cl_6 and $AmNO_3$. Vorwerk (*J. C. S.*, lii., 299).—The results are low on account of the undecomposed nitrated carbon compounds.

1224. Lucas (*J. C. S.*, lxxiv., ii., 482).—Chlorides prejudicial. Ratio of MoO_3 to Fe present should be 3 to 2, and temperature 80°.

1225. Handy and Lœffler (*J. I. S. I.*, 1894, i., 612).—P is not completely precipitated by five minutes' shaking at 25° (see 1253).

1226. Phillips and Carnahan (*J. I. S. I.*, 1814, i., 612).—Use a stream of gas or air for accelerating the precipitation of the P.

1227. Schmœger (*J. C. S.*, lxxii., ii., 230).—P is completely precipitated by Mo in the presence of citric acid.

1228. Tamm (*C. N.*, xlix., 208).—P may be imperfectly precipitated when organic acids due to combined carbon are not destroyed. Prescribes the best mode of decomposing the iron, &c. Ores must be fused in order to get all the P into solution.

1229. Wood (*C. N.*, lii., 279).—By dissolving Fe in HNO_3 and at once adding Mo, exactly two-thirds of the P is precipitated. After boiling with CrO_3, all the P is precipitated. SiO_2 need not be separated.

1230. Eggertz (*J. S. C. I.*, 1884, 179).—By merely dissolving and adding Mo as above, three-fourths of the P is precipitated. Deficiency due to existence of P other than as orthophosphate.

1231. Schneider (*J. I. S. I.*, 1893, i., 407).—The nitric acid solution is further oxidised in order to change all the P to orthophosphate, and not to destroy organic acids. $KMnO_4$ is better than CrO_3 or H_2O_2. The MnO_2 should be re-dissolved by $FeSO_4$ and not oxalic compounds.

1232. Hamilton (*J. S. C. I.*, 1891, 904).—Showing that incomplete precipitation from nitric acid solutions is not due to carbonaceous matter, but to incomplete oxidation of the P.

1233. Cheever (*J. I. S. I.*, 1884, 715; and 1885, 364).—Oxidise the iron solution with HNO_3+KClO_3, dissolve the MnO_2 in HCl, eliminate chlorine, and precipitate with Mo as usual.

1234. Reis (*J. I. S. I.*, 1887, ii., 365).—Oxidation with CrO_3 causes Cr to be occasionally precipitated with the P. Oxidise with $KMnO_4$, destroy excess with HCl, and proceed as usual. Or add $SnCl_2$ to the HCl solution of the yellow precipitate and titrate the excess with permanganate.

1235. McKenna (*J. I. S. I.*, 1894, i., 612).—Oxidation of

* AmHO added after the Am_2MoO_4 accelerates the formation of the PMo, but generally gives high results.—H. B.

chilled iron solutions with $KMnO_4$ gives lower results than evaporation to dryness.

1236. Ibbotson and Brearley (*C. N.*, lxxxii., 270)—SiO_2 removed by evaporation with acids contains some P (1206). Dissolve ferro-silicon in HNO_3+HF, and proceed as in 1348).

1237. Finkener (*C. N.*, xxxix., 42; and xlvii., 94).—Precipitate from solutions containing large amounts of $AmNO_3$, wash with very acid 20 per cent $AmNO_3$, dissolve from the paper, and expel $AmNO_3$ by gentle ignition.

1238. Troilius (*C. N.*, xliv., 299). — Dissolve in HNO_3+HCl. Expel HCl. PMo dried at 95—140°, or may be ignited so gently as to get rid of the paper without loss of weight.

1239. Meinecke (*C. N.*, liii., 53).—Add Mo at 50—60°, and allow to settle in the cold. Ignite at 400—500°; the paper separately. Residue contains 4·02 per cent P_2O_5, or, more accurately (*J. I. S. I.*, 1896, i., 540), 3·95 per cent P_2O_5.

1240. Vorwerk (*J. I. S. I.*, 1887, i., 465).—Oxidise nitric acid solution with CrO_3, and ignite PMo as 1239; ignited precipitate contains 1·754 per cent P. Si does not interfere with the precipitation of the P. Digestion with CrO_3 does not complete the oxidation of spiegels.

1241. Anon. (*C. N.*, lxii., 28).—Oxidise the nitro-sulphuric solution with CrO_3, and ignite PMo as 1239 to $P_2O_5Mo_{24}O_{68}$.

1242. Neumann (*J. C. S.*, lxxiv., ii., 454) and Sherman and Hyde (*J. C. S.*, lxxviii., ii., 757).—The PMo is ignited to $P_2O_5.24MoO_3$ by placing the platinum crucible within a porcelain one well into a Bunsen flame.

1243. Carnot (*C. N.*, xlix., 216).—All the P (in rocks, &c.) is precipitated along with some Al_2O_3 by boiling with hyposulphite and acetate. Ignite, dissolve in HNO_3, and add Mo.

1244. Lechartier (*C. N.*, xlix., 224).—Digest (soil) with aqua regia, precipitate Fe, &c., with CaO emulsion, ignite, digest with HNO_3, and precipitate solution (containing only a little iron) with Mo.

1245. Arnold (*C. N.*, xliii., 147, 186, &c.).—Fe_2Cl_6 and free HCl cause low results; in any case all the P is not precipitated unless part of the iron is removed. Recommends an acetate-Mo-Mg process.

1246. Mackintosh (*C. N.*, liii., 223).—On treating iron with HCl, all the P is not liberated as gas. Boil with SO_2, mix residue and the absorbing solution, and make acetate-Mo estimation (see 1338).

1247. Smith (*C. N.*, xlv., 195) and Macfarlane and Wilson (*J. I. S. I.*, 1893, i., 406).—Acetate-Mo, acetate-Mg, and direct precipitation with Mo processes described.

1248. Pattinson and Stead (*J. I. S. I.*, 1888, i., 181).—As, when present, may be removed by repeated evaporation with FeO in HCl, precipitation with H_2S, or adding Zn to form arsenic hydride.

1249. Benezat (*J. I. S. I.*, 1895, i., 505).—Eliminate As by evaporating ferric solution with HCl and Na_2SO_3. 0·1 per cent As does not interfere when the precipitation is made at 45° C. Compares results by direct weighing, ignition, $SnCl_2$ colour test, and $KMnO_4$ titration of the PMo.

1250. Campbell (*J. I. S. I.*, 1891, i., 436).—Oxalic acid added to HCl solution of the ore reduces As to As_2O_3, and HCl evaporation eliminates it.

1251. Pattinson (*J. C. C. I.*, 1893, 119).—Reduce solution of ore with $Na_2S_2O_3$, precipitate As with ZnS, and P from the filtrate (as ferric phosphate) with $BaCO_3$. Finish as usual.

1252. Schneider (*J. I. S. I.*, 1893, ii., 529).—As is precipitated with the P only when the solution is a nearly neutral one.

1253. Babbitt (*J. I. S. I.*, 1895, i., 134).—As is precipitated with the P beyond 25° C. At that temperature five minutes' shaking precipitates all the P, but the PMo is very finely divided.

1254. Schneider (*J. I. S. I.*, 1897, ii., 497).—A careful investigation of the best conditions for precipitating P. As comes down at ordinary temperatures; Mo in acid solutions is reduced by Zn to Mo_2O_3, but is readily re-oxidised by the air.

1255. Reis (*J. I. S. I.*, 1889, i., 396).—The rapid methods of estimating P allow very little As to contaminate the precipitate.

1256. Ridsdale (*J. I. S. I.*, 1895, i., 124).—Influence of varying amounts of As on the precipitation of PMo.

1257. Carnot and Goutal (*J. C. S.*, lxxii., ii., 520).—Treatment of the iron with neutral cupric-potassic chloride leaves all the P in the residue; As passes into solution.

1258. Jennings (*J. I. S. I.*, 1888, ii., 331).—Decompose ore with HCl, reduce with SO_2, and boil to precipitate Ti. Fuse the residue, add soluble portion to main filtrate, precipitate P along with a little Fe, and add Mo to the solution thereof as usual.

1259. Baskerville (*J. I. S. I.*, 1893, ii., 538).—Fuse titaniferous iron ore with Na_2CO_3+KNO_3, digest with water, add Fe_2Cl_6 to filtrate, and proceed as above.

1260. Pattinson (*J. S. C. I.*, 1895, 443 and 1022).—Ti interferes with precipitation of P. Add alum to FeO solution, precipitate $AlPO_4$, fuse, remove soda titanate, and precipitate P as usual. Hogg finds that Ti retards, but does not prevent, the precipitation of any P.

1261. Tamm (*J. I. S. I.*, 1887, ii., 365).—The P must be determined in the basic acetate of iron precipitated from the solution of the Fe-Mn alloy.

1262. Meinecke (*J. I. S. I.*, 1888, i., 378).—Manganese interferes in no way with the direct precipitation of P with Mo.

1263. Metz (*J. I. S. I.*, 1891, ii., 324) and Zimmermann (*J. S. C. I.*, 1893, 293).—The PMo is weighed in a specific gravity bottle; its actual weight being deduced from its known specific gravity (3·252).

1264. Ziegler (*C. N.*, lxvi., 298).—The ferro-chromium is fused with $NaNO_3$+KHO, dissolved in HCl+HNO_3, HCl eliminated, and P estimated as usual.

1265. Hempel (*J. S. C. I.*, 1890, 111).—Phosphor-tin is decomposed in a current of Cl, and P precipitated with Mo.

1266. Woodbridge (*J. I. S. I.*, 1889, ii., 476).—P exists in ores chiefly as apatite, and therefore merely boiling with nitric acid and adding Mo to the filtrate serves to estimate it.

1267. Mixer (*J. I. S. I.*, 1896, ii., 454; and 1897, ii., 509).—The P in the insoluble residue of an ore is estimated after the manner of 1270.

1268. Lychenheim (*J. I. S. I.*, 1894, i., 620).—The P of coal is all in the ash, and can be completely extracted with HCl.

1269. Campredon (*C. N.*, lxxv., 8).—The ash of the fuels must be fused with Na_2CO_3; treatment with HCl merely does not dissolve out all the P. Also Crobaugh (*J. S. C. I.*, 1893, 1061).

1270. Norris (*J. I. S. I.*, 1894, ii., 500).—Dissolve ash with HCl+HF, eliminate these with HNO_3, and precipitate with Mo.

1271. Gladding (*C. N.*, lxxvii., 32).—PMo of constant composition. Direct weighing on tared papers for large amounts; final washing with alcohol.

1272. Brunnemann (*C. N.*, lviii., 108).—Digest basic slag with mixture of acids, evaporate at 110° to remove SiO_2, take up in HNO_3, and precipitate with Mo.

1273. Loges (*J. I. S. I.*, 1887, ii., 371).—Digest basic slag with H_2SO_4 in order not to attack phosphides,

which have not the same agricultural value as phosphates. Also Kosmann (*J. C. S.*, l., 489).

1274. Klein (*J. I. S. I.*, 1886, 401 and 1024).—Decompose slag with $KNaCO_3 + KClO_3$, eliminate SiO_2, and add Mo. Boiling HCl does not attack iron phosphide.

1075. Spuller and Kalmann (*J. C. S.*, lxvi., ii., 29).—Formation of silico-molybdate is favoured by $AmNO_3$. Oxidise HNO_3 solution with $KMnO_4$, destroy excess with KNO_2, and add Mo.

1276. Crispo (*J. I. S. I.*, 1892, i., 489).—The amount of PMo formed depends on the proportion of P_2O_5, MoO_3, and N_2O_5 present. The simpler forms of the method are unreliable.

1277. Lipowitz (*C. N.*, i., 264).—Adds tartaric acid in making up the Mo reagent, so that MoO_3 may not be precipitated by an acid, by diluting, or by boiling (see 1210 and 1227).

1278. Juptner (*J. I. S. I.*, 1894, ii., 491).—As 1227. As much as 60 grms. tartaric acid per litre may be used.

1279. Veitch (*J. C. S.*, lxx., ii., 543).—The use of tartaric acid is permissible, but not advantageous.

(To be continued).

ON THE RESULTS OF A SEARCH FOR OTHER SUGARS THAN XYLOSE AND DEXTROSE IN THE PRODUCTS OF THE HYDROLYSIS OF WOOD FROM THE TRUNKS OF TREES.*

By F. H. STORER,
Professor of Agricultural Chemistry, Harvard University.

(Concluded from p. 284).

E. *Experiments in which Pure Dextrose was treated with Strong Sulphuric Acid.*—In contrast with the foregoing observations on cotton, a few experiments were made by treating pure dextrose with strong sulphuric acid, and noting the reducing and quasi-rotatory power of the products. Thus, 10 grms. of dextrose anhydride were mixed with 14 c.c. of sulphuric acid of 90 per cent H_2SO_4, and the mixture was allowed to stand for twenty-four hours. No immediate colouration occurred, but gradually the mixture turned brown, and at the end of twenty-four hours it had become black. The mixture was poured into enough boiling water to reduce the acid to a strength of 3·5 per cent H_2SO_4, and the boiling was continued for three hours. The resulting solution was almost colourless; it exhibited only a slight brown or yellowish tint which did not increase in the course of the subsequent processes of neutralisation and evaporation. There was no need of decolorising the solutions before testing their rotatory power.

One part of the product of the hydrolysis was neutralised with calcium carbonate, and evaporated to a thin syrup, which gave quasi-$[\alpha]_D = 78°61'$, and reduced enough Fehling's liquor to indicate the presence of 69·76 per cent of dextrose, calculated, of course, on the quantity of dry dextrose that was treated with sulphuric acid. A portion of this syrup was evaporated to a thick syrup, which was treated with successive portions of cold, strong alcohol until nothing more was dissolved. There was left a slimy, sticky mass similar in appearance to those obtained by similar treatment from wood and from cotton. It gave quasi-$[\alpha]_D = 73°33'$.

Another part of the acid liquor which resulted from the original hydrolysis was neutralised with lead carbonate, and the filtrate therefrom was treated with sulphuretted hydrogen; and these processes were repeated a second time for the sake of certainty. After boiling off the excess of sulphuretted hydrogen, the clear solution gave quasi-$[\alpha]_D = 66°45'$, and Fehling's liquor showed 83·39 per cent of "dextrose." The solution evaporated to a syrup, and treated with strong alcohol, in which much of it dissolved, left an insoluble residue which gave quasi-$[\alpha]_D = 88°$.

Having in view the well-known difficult solubility of anhydrous dextrose in strong alcohol, one or two experiments were made for the sake of contrasting dextrose precipitated by alcohol with the "matter insoluble in alcohol" mentioned on foregoing pages. To this end a quantity of pure dextrose anhydride (from Merck and Co.) was dissolved in water, and the solution was evaporated (without boiling) to a syrup which was treated with cold, strong alcohol. Only a part of the syrup dissolved in the alcohol, while there was left undissolved a sticky, stringy mass similar in appearance to the matter insoluble in alcohol so constantly obtained in the experiments on wood and cotton. The matter soluble in alcohol gave quasi-$[\alpha]_D = 58°1°$. The matter insoluble in alcohol was dried at 100°, and weighed. Its rotatory power (true) was found to be $[\alpha]_D$ 53·03, calculated on the weight of the solution examined. When tested with Fehling's liquor, 84·56 per cent of the original dextrose was indicated, and a rotation of quasi-$[\alpha]_D = 62°7$.

In order to be sure that the dextrose operated upon was really in the state, not of the anhydride, but of a hydrate—such as would naturally be present in the liquors obtained by hydrolysing cotton or wood—3 grms. of dextrose anhydride, dissolved in water, were boiled for some time, for the purpose of changing the anhydride to the hydrate, and the solution was evaporated to a syrup upon which a quantity of strong alcohol was poured. In this case the strong alcohol, either cold or hot, readily dissolved the larger part of the syrup. To all appearance more than three-fourths of the syrup went into solution when treated with successive portions of the alcohol, while less than one quarter of the syrup remained undissolved. It is perhaps not impossible, even in this case, that the strong alcohol may have dehydrated some of the dextrose which had been held in solution as a hydrate, and have thrown it down as an anhydride. If this conception be valid, it follows that some part of the reducing power exhibited by the "matter insoluble in alcohol," obtained from wood and cotton, may really be due to the presence of dextrose in that matter. But, on the other hand, it may equally well be true that the aqueous solution in this experiment was not boiled long enough, before it was evaporated, to change all the original anhydride to a hydrate. It is not impossible perhaps that if the aqueous solution of the dextrose anhydride had been boiled longer than it was, the conversion might have been so complete that alcohol would have dissolved everything. Lack of time has prevented me from studying this point.

Some conclusions to be drawn from the foregoing experiments may be stated as follows:—

I. When strong sulphuric acid is made to act upon cellulose, and the product is subsequently boiled in dilute acid, it is not true that the whole of the cellulose may readily be changed to dextrose. The statements made in relation to this subject in most chemical text-books are faulty in several respects.

II. It is a well-known fact that when strong sulphuric acid is made to act upon carbohydrates—that is, upon starch, sugars, dextrins, or cellulose—compounds of the carbohydrate and the acid are formed. At one time or another these compounds have been called by several different names—for example, vegeto-sulphuric acid, sulpholignic acid, sulphoglucic acid, dextrose-sulphuric acid, cellulose-sulphuric acid, &c.*—and it has been held not uncommonly that they may be decomposed pretty thoroughly by the long-continued boiling in diluted acid which occurs in the actual process of hydrolysis. In point of fact, it is by

* *Bulletin of the Bussey Institution*, 1900, vol. ii., Part 9.

* Compare Braconnot, *Annales de Chim. et de Phys.*, 1819, xii., 173; Peligot, *Annales de Chim et de Phys.*, 1838, lxvii., 113; Blondeau, *Journ. fur Prakt. Chem.*, 1844, xxxii., 429; Fehling, *Ann. der Chem. und Pharm.*, 1845, lii., 134, and lv., 13; Hoenig und Schubert, *Monatshefte fur Chem.*, 1885, vi., 702.

no means an easy matter to decompose these compounds completely by way of hydrolysis. As a general rule, no inconsiderable part of the organic matter with which the strong acid united at first is not changed to dextrose when boiled subsequently in the diluted acid. Some part of this undecomposed matter remains admixed with the dextrose-syrup, and, in experiments such as have been described above, it must necessarily tend finally to contaminate the solid dextrose obtained from the syrup.

III. In spite of the fact that solutions of salts of the above-mentioned compounds of a carbohydrate and strong sulphuric acid are highly unstable, it appears to be by no means easy to decompose such solutions *completely*. Even after long-continued boiling of dilute solutions of the calcium or barium salts of these copulated acids, some portions of the salts are apt to escape decomposition, and to contaminate the dextrose syrups. When strong alcohol is added to such syrups any remnants of the sulpho-salt which may be present will remain undissolved by the alcohol, so that a certain quantity of calcium or barium, as the case may be, will be found admixed with the organic matter.

To this cause I attribute the presence of notable quantities of inorganic matter in the syrups obtained by evaporating the neutralised liquors from the hydrolysis of woods and of cotton. In the experiments described on pages 257—258, it is evident that the processes employed for obtaining crystals, and in testing for mucic acid, and those where the acid products of a first hydrolysis were boiled a second time after the removal of the wood, did finally decompose the calcium and barium salts that were contained in the "matter insoluble in alcohol," and so liberated the sulphuric acid from its organic combination in such wise that it could now combine directly with calcium or with barium to form visible crystals or precipitates, as the case might be.

I am familiar with the fact that more gypsum can be held dissolved in solutions of sugar than in mere water. Sostman (*Zeit. des Vereins fur die Rübenzuckerindustrie des Deut. Reiches*, xvi., 517), studied this matter in 1866, and I have myself noticed the fact several years earlier (as stated in my "First Outlines of a Dictionary of Solubilities of Chemical Substances," Cambridge, 1864, p. 608, column 1). But it has seemed to me in the present experiments that the appearance of the crystals of gypsum, or what not, was a consequence of the decomposition of sulpho-compounds, by which the gypsum, or rather its components, had previously been masked.

IV. The statement of Béchamp (*Annales de Chim. et de Phys.*, [2], xlviii., 502), that on crystallising his glucose from "lignin" (presumably cotton), he got "two kinds of crystals, one hard as cane sugar, the other 'houppes,' such as those of starch sugar," is readily explained on the assumption that he had in hand crystals of inorganic matter which had resulted from the decomposition of the last portions of the calcium salt of the cellulose-sulphuric acid. In my own experiments I have, like Béchamp, obtained two kinds of crystals on evaporating my glucose syrups; but, as has been said, the hard, well-defined prisms were not crystals of sugar—they consisted solely of inorganic matter.

V. Perhaps it was with reference to the foregoing statement of Béchamp that Berthelot (*Annales de Chim. et de Phys.*, 1859, [3], lv., 293), was led to remark that "the 'glucose de ligneux,' still little known, appears to be distinct from all other glucoses," though it may be that he recognised more clearly than some of his successors have done that, until it has actually been crystallised, the dextrose obtainable from wood or cotton is a distinctly impure product.

VI. It has been taught by several chemists in recent years that (barring xylose, which may be obtained in small quantity from wood cellulose) no other sugar than dextrose is obtainable on hydrolysing cellulose with acids, and the experiments here recorded coincide with this opinion. But, in so far as relates to the *quantity* of dextrose than can be obtained from a given weight of cellulose, I find myself unable to agree with several standard authorities (compare Lippmann, "Chemie der Zuckerarten," Braunschweig, 1895, p. 104). On the contrary, I would urge, in view of the lack of purity of the dextrose syrups obtained on hydrolysing cellulose, that it is difficult to escape the conviction that most of the current statements as to the very large proportion of dextrose that may be obtained from a given weight of cellulose must have been somewhat exaggerated. For the most part, those observers who have obtained large yields of dextrose from cellulose appear to have based their statements solely on the quantity of cupric oxide reduced by the product of their hydrolysis—that is, their statements refer to the quantity of reducing matter shown by Fehling's liquor when the product of the hydrolysis came to be tested. It is seldom that any experimenter has based his declared results on a definite quantity of dextrose actually separated from the liquor and weighed. But, as the foregoing experiments show, there are contained usually in the saccharine solutions, which result from the hydrolysis of cellulose, other matters beside dextrose that are capable of reducing no inconsiderable quantities of Fehling's liquor.

VII. In the light of existing knowledge it is to be presumed that the "matter insoluble in alcohol," so constantly referred to on the foregoing pages, consist for the most part of a more or less impure "dextrin," which has resulted from the decomposition of the copulated acid that was formed in the beginning by the action of the strong sulphuric acid on the cellulose. The general appearance of the substance now in question, and some of its properties, seem to show a strong family resemblance to the dextrins proper, though the fact that it exhibits a higher reducing power than the true dextrins, fosters a lingering suspicion that it may possibly contain an amorphous sugar analogous with, or even akin, in one sense, to, isomaltose (gallisen). It is not impossible, indeed, that the mere act of adding strong alcohol to the syrup obtained on evaporating the neutralised product of a hydrolysis may serve to dehydrate a small portion of the dextrose in that solution—that is to say, some dextrose-anhydride may perhaps be formed, and as this substance is but little soluble in absolute alcohol, enough of it might remain in the precipitate to account for the reducing action which solutions of the precipitate exhibit. However this may be, it is manifest that the major part of the precipitate insoluble in alcohol is a body of the same order as those which Hoenig and Schubert (*Monatshefte fur Chem.*, 1885, vi., 708, and 1886, vii., 474), have described as dextrins in their very elaborate research; and it especially resembles the "dextrin de ligneux" that was obtained long ago by Béchamp (*Annales de Chim. et Phys.*, [2], xlviii., 463, and especially 1856, [3], xlvi., 352; see, also, in *Comptes Rendus*, 1856, xlii., 1213, and 1860, li., 256), by means of a method almost precisely similar to my own. Béchamp treated cotton or wood with strong sulphuric acid, to which he subsequently added much water, and after thoroughly boiling the diluted liquor he neutralised it with calcium carbonate, and evaporated the filtrate to a syrup. By means of strong alcohol he separated the "dextrin de ligneux" from the syrup, while dextrose went into solution in the alcohol, and was crystallised therefrom. The wood-dextrin thus obtained must have been contaminated like my own with small quantities of a calcium salt. It gave him a specific rotation of $[\alpha]j = 88{\cdot}9°$ * while that of dextrin made from starch was $[\alpha]j = 176°$, and that of soluble starch was $[\alpha]j = 211°$.

By an unfortunate typographical error in Béchamp's article, as published in the *Comptes Rendus*, li., 256—that is, by the mere misplacing by the printer of a character representing a bent arrow in such wise that the arrow was made to point to the left instead of to the right—it was there made to appear that the rotation of the wood-

* If it be admitted, with Brown and Heron (*Journ. Chem. Soc.*, London, 1879, xxxv., 605), that $[\alpha]j : [\alpha]D :: 24 : 21{\cdot}54$, then $[\alpha]j = 88{\cdot}9° = [\alpha]D = 79{\cdot}79°$.

dextrin is to the left, though a careful reading of the context shows clearly enough that Béchamp meant to assert that the rotation of this substance is really towards the right hand. It is to be noted, moreover, that Béchamp was one of the last men in the world to speak of a left-handed *dextrin*; for he worked at a time when the word "dextrin" was new, and he had always in mind the derivation and the real meaning of the word. In his memoirs he refers repeatedly to the fact that the substance named "dextrin" by Biot was really not the substance known as "dextrin" in commerce, but an impure soluble starch (now often called amylo-dextrin). The misprint was copied unwittingly into several standard works,* where it has remained an effective stumbling-block to perturb the unwary.

VIII. The difficulty of studying the products of the hydrolysis of cellulose is manifestly increased by the fact that not only do "dextrins" result from the splitting up of the copulated compounds formed by the union of strong sulphuric acid with carbohydrates, but that phenomena of reversion of dextrose to dextrin may occur in the process of dextrose to dextrin may occur in the process of hydrolysing with diluted acids. What connection there may be between the dextrins thus formed by reversion of dextrose and those obtained by the breaking down of cellulose-sulphuric acid, appears to be still an open question. It has been reported merely that the reducing and rotatory powers of the former are lower than those of the latter.

I am greatly indebted to my assistant, Mr. Winfred W. Braman, for his careful attention to the performance of many tedious and discouraging details of manipulation, which have had to be worked out in the course of this investigation.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MAY 31ST, 1901.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, June 10th, 1901.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 208 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from May 1st to May 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

* See, for example, the Cavendish Society's Edition of L. Gmelin's "Handbook," xv., 188; and Watts' "Dictionary of Chemistry," 1866, ii., 313, 314. So, too, in the 1862 (German) Edition of Gmelin's "Handbuch," vii., 633, where the error was evidently copied from from the English Edition. It is noteworthy that the editor of the *Journal fur Praktische Chemie* on translating, for publication in his journal (1861, lxxxii., 121), Béchamp's article at the time of its appearance, corrected the misprint, though without comment. Hence the error does not appear in those German treatises which have taken their information from the *Journal fur Praktische Chemie*.

Of the 208 samples examined by us during the month, all were found to be clear, bright, and well filtered.

Again we have to record a deficiency in the rainfall; rain fell at Oxford on seven days only, when 1·24 inches were measured, more than 1 inch falling on the 6th, 7th, 8th, and 9th. The average for thirty-five years is 1·75 inches, leaving a deficit of 0·51 inch; this, added to the previous deficit of 1·21 inches, brings it to 1·72 inches, or 19·7 per cent for the year.

Our bacteriological examinations of 538 samples have given the results recorded in the following table; we have also examined 53 other samples, from special standpipes, &c., making a total of 591 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	106
New River, filtered (mean of 128 samples) ..	6
Thames, unfiltered (mean of 26 samples) ..	852
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 293 samples)	9
Ditto ditto .. .. highest	112
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 26 samples) ..	209
River Lea, from the East London Company's clear-water wells (mean of 39 samples) ..	13

Of the 460 samples of impounded and filtered water supplied to London, examined bacteriologically during the past month, seventy samples, or 15·2 per cent, were sterile. Only one sample out of the total number examined contained more than 150 microbes, and only three, or 0·6 per cent, contained more than 100 microbes per c.c. The mean of the microbes in the three excess samples was 147, against a corresponding mean last month of 126.

Within our experience the London water has never been in a purer or more satisfactory condition than during this month. It must be remembered, however, that for some months past there has been exceedingly little rain, and consequently the river Thames has been supplied mainly by spring water from the chalk.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 6th, 1901.

Prof. THORPE, C.B., F.R.S., Vice-President, in the Chair.

MESSRS. Oldershaw, Martin, Jemmett, Dunstan, Bousfield, Taylor, Goltz, and Hyder were formally admitted Fellows of the Society.

The following certificates were read for the first time:—Samuel Irwin Crookes, Thanet Street, Clay Cross, Chesterfield; Herbert Blackmore Hammond, 3, Vicar's Close, Lichfield; Christian Müller, 10, Selwyn Avenue, Richmond, S.W.; Rowland Samuel Potter, 2, Museum Hill, Haslemere; Robert Stephenson, jun., Burwell, Cambridgeshire: Frank Wade, 36, Craven Park, Harlesden, N.W.; Morton Wager, 5, Wilton Street, Batley.

Of the following papers, those marked * were read:—

*93. "*A Laboratory Method for the Preparation of Ethylene.*" By G. S. NEWTH.

By substituting tribasic phosphoric acid for sulphuric acid in the ordinary process for obtaining ethylene, this gas may be prepared in a high state of purity. Syrupy phosphoric acid is boiled in a flask until the temperature reaches 200°, when ethyl alcohol is delivered drop by drop

to the bottom of the boiling liquid. If the temperature is maintained about 220°, an abundant evolution of the gas takes place. As the liquid does not char or froth up, the operation may be conducted in a small reaction vessel; and as the gas is entirely free from carbon dioxide, and of course from sulphur dioxide, it is not necessary to wash it.

The liquid products of the reaction, consisting of water, ether, unchanged alcohol, and a small quantity of an oily liquid, are collected in a vessel cooled by ice, the ethylene passing on practically pure.

By acting in a similar manner upon methyl alcohol, the gas evolved is pure methyl ether; from propyl alcohol, propylene is produced. In the case of the normal alcohol, a temperature about 250° is required to bring about the decomposition, whilst the secondary alcohol splits up rapidly at 210°.

•94. "*Oroxylin.*" By W. A. H. Naylor and C. S. Dyer.

The authors described the methods of isolation and purification of oroxylin, a yellow, crystalline substance obtained from *Oroxylum Indicum*.

Its chief decomposition product, through the action of caustic alkali of different strengths, is benzoic acid, but if the reagent be applied in the cold and in the form of a weak solution, the primary product is benzaldehyde. With bromine it forms a dibromo-derivative which crystallises in needles melting at 175°; on acetylation a triacetyl derivative is obtained which crystallises in colourless needles melting at 150°. The authors conclude that oroxylin contains three hydroxyl groups, a loosely attached benzene nucleus, and they assign to it the formula $C_{19}H_{14}O_6$.

•95. "*The Constitution of the Acids obtained from α-Dibromocamphor.*" By A. Lapworth and W. H. Lenton.

When tribromocamphonolactone (*Trans.*, 1900, lxxvii., 458), is hydrolysed with alkali, and the product oxidised with cold sodium hypobromite, a mixture of acids is obtained from which trimethylsuccinic acid and a small quantity of camphoronic acid have been isolated. The greater portion of the mixture, however, consists of a dibasic lactonic acid, $C_9H_{12}O_6$, which has been identified with the acid hitherto known as β-hydroxycamphoronic acid.

The authors conclude that when bromocamphoronic acid is converted into α-monobromocampholid, the lactonic oxygen becomes attached to the ring at the δ-position with regard to the carboxyl group, instead of at the γ-position as was at first thought probable (*Trans.*, 1899, lxxv., 1139), the only possible formula for camphonic acid being—

$$CO_2H\cdot CMe\begin{cases}CH_2—CH_2\\CMe_2\cdot CH_2\end{cases}>CO.$$

Bromocamphorenic acid and camphononic acid must be represented by the formulæ—

$$CO_2H\cdot CMe\begin{cases}CH_2\cdot CH_2\\CMe_2\cdot CH\end{cases}=CBr$$

and—

$$CO_2H\cdot CMe\begin{cases}CH_2—CH_2\\|\\CMe_2\cdot CO\end{cases}$$

respectively.

The formulæ thus arrived at are in complete accordance with the properties of the compounds, and it is now easy to understand the great difference in the reactivities of the carbonyl groups of camphonic acid and camphononic acid. The change induced in α-dibromocamphor by moist silver compounds must be represented by the scheme—

$$\begin{array}{l}CH_2\cdot CH—CBr_2\\|\quad\quad|\\CMe_2\\|\\CH_2\cdot CMe—CO\end{array}+H_2O=\begin{array}{l}CH_2\cdot CBr:CH\\|\quad\quad|\\CMe_2\\|\\CH_2\cdot——\cdot CMe\cdot CO_2H\end{array}+HBr,$$

and the authors suggest that an intermediate compound containing a trimethylene ring may be formed. Such an assumption is possibly applicable to many other changes in the camphor and terpene series, including the apparent migrations of methyl groups from one carbon atom to an adjacent one (a type of change otherwise without real analogy), and the formation of camphene derivatives from bornyl chloride and allied compounds (compare Marsh, *Proc.*, 1899, xv., 54).

•96. "*The Decomposition of Chlorates.* IV. *The supposed 'Mechanical' Facilitation of the Decomposition of Potassium Chlorate.*" By W. H. Sodeau, B.Sc.

The supposed analogy between the decomposition of potassium chlorate and the boiling of water, in respect of the facilitating action of certain powders, is invalidated by the fact of the former not being appreciably facilitated by reduction of pressure to 1 m.m. (*Trans.*, 1900, lxxvii., 144). There would seem to be a possibility of chemical action with all substances known to produce a marked effect on the rate of decomposition of potassium chlorate.

From an experiment in which 1 per cent of barium sulphate was added and a 500 per cent increase of rate observed, Veley concludes that "chemically inert" powders facilitate the decomposition (*Phil. Trans.*, 1888, clxxix., [A], 270).

The author has studied the effect of adding 1 per cent of barium sulphate, and finds that the average increase of rate amounts to only 16 per cent. There is evidence of the formation of a little barium chlorate, by double decomposition, and this would appear to account for the slight facilitation observed.

It is concluded that the supposed ability of chemically inert solid particles to facilitate the decomposition of potassium chlorate is unsupported by experimental evidence, and, if actually existent, is inadequate to explain even a small fraction of the effect of the oxides of manganese, iron, cobalt, nickel, and copper. The action of these latter substances would, therefore, appear to be entirely chemical.

•97. "*On the Action of Sodium Methoxide and its Homologues on Benzophenone Chloride and Benzal Chloride.*" By J. E. Mackenzie, D.Sc., Ph.D.

The author has already (*Trans.*, 1896, lxix., 985), described the preparation of dimethoxy-, diethoxy-, and dibenzoxy-diphenylmethanes by the action of sodium meth-, eth-, and benz-oxide respectively on benzophenone chloride. To these are now added *dipropoxydiphenylmethane*, $(C_6H_5)_2C(OCH_2\cdot CH_2\cdot CH_3)_2$, colourless, prismatic crystals, m. p. 33—34·5°; *diisobutoxydiphenylmethane*, $(C_6H_5)_2C[OCH_2\cdot CH(CH_3)_2]_2$, m. p. 36—38°, readily splitting up in accordance with the equation—

$$(C_6H_5)_2C[OCH_2\cdot CH(CH_3)_2]_2=$$
$$=(C_6H_5)_2CO+[(CH_3)_2CH\cdot CH_2]_2O;$$

4 : 4′-dihydroxytetraphenylmethane, $(C_6H_5)_2C(C_6H_4OH)_2$, which is formed instead of the diphenoxy-compound, $(C_6H_5)_2CCl_2+2C_6H_5ONa=(C_6H_5)_2C(C_6H_4OH)_2+2NaCl$, crystallises from ethereal solution with two molecules of ether of crystallisation, and melts at 285—287°. It gives a *diacetate*, $(C_6H_5)_2C(C_6H_4OCH_3CO)_2$, m. p. 170—171°. Experiments on the action of ethyl alcohol, and of 1 per cent alcoholic solution of hydrochloric acid on benzophenone gave negative results.

Nitration of dimethoxydiphenylmethane resulted in the formation of 4 : 4′- and 3 : 3′-dinitrobenzophenones, whilst aniline split it up, forming diphenylmethylene anilide.

The action of sodium methoxide, ethoxide, and benzoxide on benzal chloride at the ordinary pressure was tried. The first and second actions proceed as described by Wicke (*Ann.*, 1857, cii., 356), dimethoxy and diethoxybenzylidene being formed. From the benzoxide experiment the only substance isolated was stilbene. By heating phenol itself with benzal chloride, condensation took place as follows,—

$$C_6H_5\cdot CHCl_2+2C_6H_5OH=C_6H_5\cdot CH(C_6H_4OH)_2+2HCl,$$

the substance formed being identical with 4 : 4′-dihydroxy-

tetraphenylmethane (*Ber.*, 1889, xxii., 1944), and giving the same diacetyl derivative.

When similar experiments were made under pressure, the action was found to be quite different from the above, and may be expressed generally thus:—

$$R'ONa + C_6H_5{\cdot}CHCl_2 = R'Cl + C_6H_5{\cdot}CHO + NaCl.$$

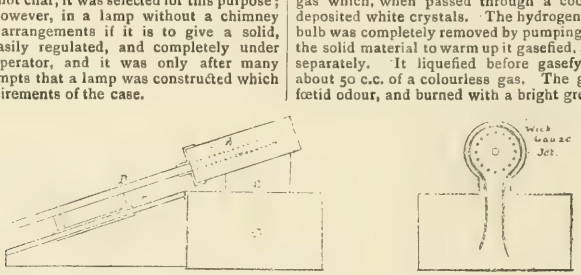
In this manner, methyl, ethyl, propyl, and benzyl chlorides were obtained.

When sodium ethoxide acts on ethylene dibromide under pressure, acetylene is produced.

*98. "*A Kerosene Oil Blowpipe.*" By A. RICHARDSON, Ph D.

This blowpipe has been devised in order to utilise the combustion of kerosene oil for the production of a blowpipe flame, suitable for glass blowing and other purposes, so as to combine the advantages of a gas blowpipe while independent of a supply of gas. The need of such a blowpipe is obvious in a country like India, where gas is not always available, and where in many college laboratories not supplied with gas blowpipe work is necessarily limited to operations with the mouth blowpipe and spirit lamp.

At first it seemed possible to use one of the vegetable oils, such as cocoanut oil, by burning it in a modified form of glass-blower's "tallow lamp," but the tendency of all such oils to char at the temperature of the blowpipe flame renders them useless as a continuous source of heat unless the wick is being constantly trimmed. As kerosene oil does not char, it was selected for this purpose; its combustion, however, in a lamp without a chimney requires special arrangements if it is to give a solid, steady, flame, easily regulated, and completely under control of the operator, and it was only after many unsuccessful attempts that a lamp was constructed which fulfils all the requirements of the case.



As it now stands, the blowpipe consists of a metal tube, A, 1½ inches long and ⅝ of an inch in diameter, fixed at an acute angle above the oil holder, B, with which it is connected by a flattened tube or wick holder, C. A wick about 1 inch wide passes from B through C, round the inside of A, and back to B, leaving the central portion of the tube open. The wick is protected and kept in its place by a tube of iron wire gauze projecting beyond the wick on either side. The lower end of A is closed by a perforated cap, through the centre of which the blowpipe jet, D, passes. This is made to slide backwards and forwards on the rail, E, so that its position in the centre of the tube can be regulated.

A thread of asbestos dipping in the oil passes up the wick-holder, and projects just in front of the wick at the open end of A.

To use the lamp the asbestos thread is first lighted; this furnishes a small flame at the mouth of A; if now the bellows be worked, combustion takes place within A on the surface of the gauze. The size of the flame depends on the position of the jet, since combustion is practically limited to that portion of the wick exposed to the air current; thus when the jet is pushed up to the open end, a fine-pointed flame is produced; as it is drawn back into the tube, the flame increases in size, giving a roaring flame when the whole length of the wick is exposed. On stopping the air supply the flame immediately subsides to its original size, and burns quietly at the mouth of the tube. In this way the flame is under complete control, and gives no trouble when not in use.

Experience has shown that the wick remains in good condition for a long time; in one case it was found to be only superficially blackened after the blowpipe had been in use for several weeks.

The dimensions given above are those which the author has found most useful for general purposes, but with a wick 2 inches wide, contained in a tube of 1 inch bore, a much larger and more powerful flame is obtained, suitable for large pieces of glass blowing, although it is not so easily regulated for the production of a small flame.

The efficiency of the blowpipe has been proved by long use; with its aid all the ordinary glass blowing which before was out of the question without gas may be done.

*99. "*Preliminary Note on Hydrides of Boron.*" By W. RAMSAY and H. S. HATFIELD.

Since Jones and Taylor investigated the product of the action of hydrochloric acid on magnesium boride (*Trans.* 1881, xxxix., 213), no work seems to have been done on the subject. The ease with which gases can be liquefied and solidified by means of liquid air made it probable that an attempt to isolate boron hydride by cooling the gas from magnesium boride would be successful.

The magnesium boride obtained for the first experiment was made by heating together boron trioxide and magnesium powder in a wrought-iron crucible on an ordinary fire. The friable, black mass, treated with concentrated hydrochloric acid in a vacuous flask, gave off a gas which, when passed through a cooled wash-bottle, deposited white crystals. The hydrogen remaining in the bulb was completely removed by pumping, and on allowing the solid material to warm up it gasefied, and was collected separately. It liquefied before gasefying, and yielded about 50 c.c. of a colourless gas. The gas had a strong, fœtid odour, and burned with a bright green flame.

Its density was 19·36; for a bulb of 32·04 c.c. capacity contained 0·0432 grm. of the gas at 605·9 m.m. pressure and 12·2°. When sparks were passed through the gas, it was decomposed, a filament of boron joining the electrodes, and conducting the current. It was found most convenient to commence the operations with a jar and spark-gap interposed, and when considerable decomposition had taken place to finish up with an "electric flame," that is, removing the Leyden jar. With the intermittent spark, the filaments were ruptured and fell; and with gas largely decomposed, they were no longer formed.

A quantitative experiment showed that the increase of volume, on decomposition, was from 2 to 3; for 19·1 c.c. of gas at 12° increased, after decomposition, to 28·1 c.c. at 11·5°. The ratio between these numbers is 2 to 2·94. This sample of gas had been exposed to the action of solid potassium hydroxide for twelve hours; it had previously passed over soda-lime and phosphoric anhydride. An attempt was made to collect the boron which separated out from another sample of 26·8 c.c. on decomposition, but it was not possible to collect it free from mercury. However, it was washed out by help of ether, the ether was removed by evaporation, and the mercury was distilled off in a current of hydrogen. The residue weighed about 0·05 grm., a number not greatly differing from 0·045, the weight of the gas. The experiment was a difficult one, and could not be expected to furnish very accurate results.

These experiments render it probable that the gas consisted mainly of a compound, B_2H_3. This gas is practically insoluble in water; it is fairly stable.

The hydrogen which passed through the cooled wash-bottle burned with a green flame; a porcelain lid held in the flame was not stained with boron, as stated by Jones and Taylor. Even when the gas was passed through a red-hot glass tube filled with fragments of unglazed clay, it still burned with a green flame, and the white clay was hardly stained. A quantity of the uncondensable gas was collected in a vacuous receiver (for it appeared to be somewhat soluble in water), and it was concentrated by diffusion through tobacco-pipe stems. Several hundred c.c. of the diffused gas were passed through a vessel, cooled by liquid air boiling under low pressure, and the gas was subjected to a pressure of 2 atmospheres, so as to reduce the volume occupied by the diluent hydrogen. A small amount solidified, but it was not possible to reduce the pressure much without its volatilising. The density of this sample of gas was 2·59, for 32·04 c.c. at 16·5° and 758·6 m.m. weighed 0·0071 grm. On the assumption that its formula is BH_3, 26·5 per cent of the sample consisted of that gas; the remainder was hydrogen. Of this mixture, 7·45 c.c. were sparked for two hours, and deposited boron on the platinum electrodes. The volume after sparking was 8·50 c.c., an increase of 1·05 c.c. Now, 26·5 per cent of 7·45 is 1·97; hence the increase of volume was in the ratio 1·97 : 3·02, a sufficiently close approximation to 2 : 3.

Other attempts to prepare the compound B_2H_3 have not been so successful. The condensable gas has, up to now, consisted of a compound decomposable with increase of volume on addition of solid potassium hydroxide, or of concentrated sulphuric acid. The density of this sample was found to be 18·1 for the weight of 32·01 c.c. measured at 16·4°, and 479·0 m.m. was 0·0187. It also deposited what appeared to be boron on sparking. There appear, therefore, to be two compounds of the formula B_2H_3, one relatively stable, the second unstable, and easily changed by reagents. The yields in the last case have been very poor, and the authors have not yet secured the conditions for producing the stable compound with certainty, uncontaminated by the unstable gas.

If it may be permitted to speculate regarding the hydrides of boron, it is probable that the following are capable of existence :—

BH_3. $H_2B{-}BH_2$. $H_2B{-}BH{-}BH_2$. Saturated.

$HB{=}BH$. $H_2B{-}B{=}BH$. Unsaturated.

cyclo-Saturated.

cyclo-Unsaturated.

The authors are inclined to suspect that the stable compound of the formula B_2H_3 is the *cyclo*-compound, to which the name *cyclo*triborene appears applicable; it is possible that triborene is the unsaturated compound, of which the formula is given above. The last formula given is the hydrogen analogue, in all probability, of the calcium, strontium, and barium borides described by Moissan and Williams (*Comptes Rendus*, 1897, cxxv., 629).

The residues left after treatment of the magnesium boride with acid, when washed and dried, give off torrents of gas on being heated; this gas consists, for the most part, of hydrogen, and contains only a trace of boron. It no doubt results from the decomposition of solid hydroborons, but the authors have not yet succeeded in separating them from the boron with which they are mixed.

100. "*On some Relations between Physical Constants and Constitution in Benzenoid Amines.*" Part II. By P. GORDAN and L. LIMPACH.

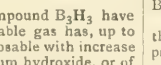
By the substitution of the benzenic hydrogen in formyl and acetyl anilides by methyl groups thirty-eight compounds can be obtained. These compounds may be arranged, or classified, according to the number ρ of the substituting groups, and also according to their relative positions—isomerides. The mode of dependence of their melting-points may be seen by comparing their experimentally determined values. The mean, D, of the melting-points of an isomeric series may be calculated from ρ. In each isomeric series there is at least one member the melting-point of which is identical with the mean value or differs very little from it. The melting-points of the others differ evenly in two directions (higher or lower) from D, and in such manner that where one compound has a melting-point considerably above D, another compound, of the same series, has a melting-point as much below D. For instance, in the acet-toluide series the mean D = 106·5. This is practically the melting-point of 1 : 2-acet-toluide (107°). The 1 : 3-compound melts at 65·5°, and the 1 : 4 at 147°, the latter compound therefore melting 40·5° higher, and the 1 : 3, 41° lower than the mean D.

The melting-points are higher when both ortho-positions are occupied, and lower when meta- or meta- and para-positions are occupied. The melting-point seems to be mainly determined by the ortho- or neighbouring position. This observation or view is borne out by the theory of "invariants."

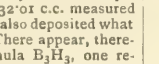
101. "*Condensation of Phenols with Esters of the Acetylene Series. V. Homologues of Benzo-γ-pyrones.*" By S. RUHEMANN.

In continuation of his research, the author has studied the behaviour of the esters of chlorofumaric and phenylpropiolic acids towards thymol and carvacrol, and thus obtained the following compounds:—

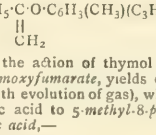
Ethyl β-thymoxycinnamate, —



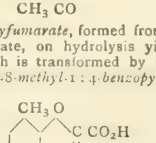
the corresponding *acid* (which decomposes at 138°), and *β-thymoxystyrene*,—



The product of the action of thymol on ethyl chlorofumarate *ethyl thymoxyfumarate*, yields on hydrolysis the *acid* (m. p. 215° with evolution of gas), which is condensed by strong sulphuric acid to *5-methyl-8-propyl-1 : 4-benzopyrone-2 carboxylic acid*,—



Ethyl carvacroxyfumarate, formed from carvacrol and ethyl chlorofumarate, on hydrolysis yields the corresponding *acid*, which is transformed by strong sulphuric acid into *5-propyl-8-methyl-1 : 4-benzopyrone-2-carboxylic acid*,—



(m. p. 237—238° with decomposition). This, on heating, loses carbon dioxide, and yields *propylmethyl-1 : 4-benzopyrone* (m. p. 59—60°).

102. "*Gum Tragacanth.*" By C. O'SULLIVAN.

The proximate constituents of the gum have been isolated, and the following were described :—

Cellulose.—The constituent insoluble in boiling water and cold dilute acid and alkalis. Treated with boiling dilute sulphuric acid, it yields arabinose, and a residue of a cellulosic nature still. This residue on further treatment

with ammonia and bromine gradually dissolves, leaving no residue of normal cellulose.

Soluble Gum.—A series of gum acids of the nature of the geddic acids were prepared. They are lævorotatory, however, the rotation being about as much to the left as that of the geddic acids is to the right. The acids are shown to be polyarabinan-trigalactan-geddic acids, the chief of them being $11C_{10}H_{16}O_{8}.3C_{12}H_{20}O_{10},C_{23}H_{36}O_{20},H_2O$. The optical activity of this acid is $[\alpha]=-88°$. Its barium salt yields 3·29 per cent BaO, against 3·23 per cent required. On sulphuric acid hydrolysis, it should yield 71·7 per cent arabinose. Quantities varying between 72 and 76 per cent moderately pure arabinose were obtained from the mixed gum acids.

Granules.—The granules, apparently starch-granules, are coloured blue by iodine, and on treatment with diastase yield dextrose, but not maltose.

Nitrogenous Matter.—No attempt was made to purify this substance. It is of much the same nature as the nitrogenous matter described in dealing with the geddic gum (*Trans.*, 1891, lix., 1061), but it does not give the same proteid reaction as that substance does.

Bassorin was not completely purified, but it was found to be an acid having $[\alpha]_D = +98°$; the neutral barium salt contains 9·2 per cent BaO. Under the action of excess of alkali it yields two acids, α- and β-tragacanthan-xylan-bassoric acid. The nature of this transformation will be described on a future occasion.

α-Tragacanthan-xylan-bassoric Acid.—Its preparation and purification were described; it is soluble in cold water. Its analysis led to the formula $C_{24}H_{34}O_{20},H_2O$. $[\alpha]_D = +138\ 6—138·2°$; $D = 4·12—4·13°$. Barium, calcium, and silver salts were prepared; the silver salt is the most insoluble, the calcium salt least. The neutral barium salt gave 19·21 per cent BaO, the calcium salt 8·24 per cent CaO, and the silver salt 22·2 per cent Ag. $C_{24}H_{34}O_{20},BaO$, requires 19·24 per cent BaO, the calcium salt 8·02 per cent, and the silver salt 24·77 per cent. In consequence of decomposition it was not possible to prepare the silver salt with any degree of satisfaction.

Digested for twenty minutes at 98° with 5 per cent sulphuric acid, it yields a lævorotatory pentose, *tragacanthose*, $[\alpha]_D = -30°$ approx., and *xylan-bassoric acid*, $[\alpha]_D = +200°$, the barium salt yielding 22·5 per cent BaO. The equation—

$$C_{24}H_{36}O_{21} + H_2O = \underset{\text{Tragacanthose.}}{C_5H_{10}O_5} + \underset{\text{Xylan-bassoric acid.}}{C_{19}H_{28}O_{17}}$$

represents the hydrolysis. $C_{19}H_{26}O_{16}O_{16},BaO$ requires 23·07 per cent BaO.

Xylan-bassoric acid is almost insoluble in cold water, the alkaline salts are soluble, salts of the alkaline earths and most heavy metals are insoluble. Acted upon with 5 per cent acid, *xylose* and *bassoric acid* are obtained.

$$C_{19}H_{28}O_{17} + H_2O = \underset{\text{Xylose.}}{C_5H_{10}O_5} + \underset{\text{Bassoric acid.}}{C_{14}H_{20}O_{13}}.$$

Bassoric acid is almost insoluble in cold water; in alkaline solution its optical activity was found to be $[\alpha]_D = +255°$, and the barium salt yielded 28—29 per cent BaO. $C_{14}H_{18}O_{12},BaO$ requires 28·8 per cent BaO.

β-Tragacanthan-xylan-bassoric acid is left behind as a crumbly mass, when the α-acid is dissolved out by cold water. On combustion it yields the same numbers as the α-acid. In alkaline solution $[\alpha]_D = +163—164°$. The barium and calcium salts, as well as most of the salts of the heavy metals, are of very low solubility. Treated with sulphuric acid, it yields the same products as the α-acid.

In a future paper, the author hopes to be able to describe bassorin more fully, as well as its conversion into the two acids described, also the two acids themselves, and particularly the products of their hydrolysis, the sugar tragacanthose, and the final acid, bassoric acid.

103. "*Optically Active Dimethoxysuccinic Acid and its Derivatives.*" By T. Purdie, F.R.S., and J. C. Irvine, B.Sc.

By alkylating methyl, ethyl, and propyl tartrates by means of silver oxide and methyl iodide, the authors have obtained the corresponding optically active dimethoxy-succinates. The methyl ester is crystalline (m. p. 51°, $[\alpha]_D\ 60° = +82·52°$); the ethyl and propyl esters are liquids, giving $[\alpha]_D\ 20° = +89·96$, $[\alpha]_D\ 60° = +85·39°$, and $[\alpha]_D\ 20° = +84·92°$, $[\alpha]_D\ 60° = +81·03°$ respectively. Dimethoxysuccinic acid is crystalline (m. p. about 151°), and gives in aqueous solution of varying concentration $[\alpha]_D\ 20° = +72·28°$ to 76·63°, in acetone +89·29° to 95·80°. The optical activity of aqueous solutions of the diamide and of various metallic salts has also been examined.

Certain regularities in the relations of the rotations of ethereal mono- and di-alkyloxysuccinates and of the corresponding acids and metallic salts were discussed, as well as Frankland's views (*Trans.*, 1899, lxxv., 347), concerning the probable cause of the maximum specific rotation exhibited by the series of ethereal malates and lactates.

104. "*The Influence of Solvents on the Optical Rotation of Ethereal Dimethoxysuccinates and Tartrates.*" By T. Purdie, F.R.S., and W. Barbour, M.A., B.Sc.

To determine whether any change of configuration is produced by alkylating the tartaric esters with silver oxide and alkyl iodide, tartaric acid was regenerated from dimethoxysuccinic acid by heating the latter with hydriodic acid; *d*-dimethoxysuccinic acid yielded *d*-tartaric acid.

The rotations of methyl, ethyl, and propyl dimethoxy-succinates in water, methyl alcohol, and benzene at varying concentrations were determined, and for purposes of comparison some observations were made on solutions of the corresponding tartrates; the latter were not proceeded with further, so as to avoid interference with the work of T. S. Patterson (*Trans.*, 1901, lxxix., 167, 477). In general the rotations of the former esters are influenced less by solvents than those of the latter, and in most cases the action is oppositely directed.

The authors pointed out that the direction of the effects of a solvent on the rotations of the members of a homologous series is often reversed on ascending the series, and they connect this with the corresponding reversed effect of the addition of CH_2 to successive terms.

From molecular weight determinations of the esters in water and benzene, more particularly from the results obtained with benzene solutions of the tartrates, the conclusion is drawn that the aggregation of disymmetric molecules is not a predominant factor in the influence of solvents on rotation.

To ascertain whether their observations support the theory of Patterson (*loc. cit.*) on the connection between rotation and molecular solution volume, the latter constants were calculated for a number of the solutions examined, but the results are inconclusive. In addition to the factors pointed out by Patterson which may mask this connection, the authors suggest another phenomenon, probably of frequent occurrence, which they think may interfere with the relationship in question.

PHYSICAL SOCIETY.

Ordinary Meeting, June 14th, 1901.

Prof. S. P. Thompson, President in the Chair.

A paper on "*Herr Jahn's Measurements of the Electromotive Force of Concentration Cells*" was read by Dr. Lehfeldt.

Prof. D. Jahn has recently published measurements of E.M.F.'s of concentration cells from which he has endeavoured to show that the law of dilution is applicable to strong solutions. The author points out that his conclusions are based on argument in a circle, because Ostwald's law is assumed in the formula used by Jahn for calculating degrees of concentration. The formulæ of Nernst and Arrhenius do not yield consistent results, and

it is suggested that the former is suitable for calculating concentrations, and the latter for calculating osmotic pressures.

A paper on "*The Mechanism of Radiation*" was read by Mr. J. H. Jeans.

This paper contains an attempt to obtain answers to two questions:—(1) What inferences can be drawn as to the mechanism by which radiation is emitted from an examination of the formula of physical optics? and (2) Is it possible with the help of these inferences to frame any conception of matter which will give a consistent account of the various optical phenomena? Starting with general spectroscopy the author has written down the radiation due to a single rotating molecule vibrating harmonically. The effect of a number of molecules is deduced, and it is shown that the condition that the continuous banded spectrum shall be absent is that either the period of rotation must be large compared with the period of vibration or the radiation from a molecule must be spherically symmetrical. Passing on to dispersion, even if the radiation is continuous between collisions, there will be a discontinuity at every collision, and the train of waves will be no longer regular. It is customary to assume that the vibrations of a dispersing medium are sympathetic with the irregular incident light. The author has calculated the ratio between forced and free vibrations in a prism or grating, and finds that if the dispersion is to be regular the vibrations must be only slightly influenced by collisions, and this requires, as in the former case, that either the period of rotation is large compared with the period of vibration or the radiation is spherically symmetrical. As this is not the case with molecules the author thinks that the line spectrum is emitted by atoms, that these atoms must be dissociated, and that the shape of these atoms is one of spherical symmetry. It is shown that if an atom is an electromagnetic system, similar to a planetary system, then the periods of such an atom would not be fixed, and there would be no reason for a line spectrum. The normal atom is therefore regarded as an electrostatic system, with some law of force, other than the inverse square law, holding at interionic distances. Such an atom when at rest would give a pure line spectrum. Rotation of such an atom causes the lines of the spectrum to shift towards the red, and as the rotation is different for different atoms the lines will not only be shifted but broadened. To calculate the periods of vibration of an atom the author has assumed it to consist of an infinitely great number of infinitely small ions. The spectrum of this consists of a collection of spectrum series, each possessing a definite head, and capable of explaining doublets, triplets, &c. It is shown that under the action of a magnetic field a line may separate out into approximately equidistant lines, the central line maintaining its position. In conclusion, the author points to many other physical phenomena which can be explained by the theory described.

The Chairman then exhibited some specimens of Jena glass. In describing these reference was made to a diagram showing the refractive index, dispersion between the C and F lines, and the reciprocal of the dispersive power of any piece of glass. For this latter quantity the symbol "ν" is used, and it was suggested to call it the achromatic refractivity of the glass. The introduction of barium increases the deviation, but leaves the dispersion unaltered. It is possible now to get crown glass with a higher refractive index than flint glass, and this makes it possible to construct an achromatic lens which will also give a flat field. It is usual in making achromatic objectives to make them accurately achromatic for the red and violet rays. A better effect can be obtained by having approximate achromatism throughout the length of the spectrum. This is achieved by matching the irrationality of one glass by means of another, and then constructing an achromatic pair with these two glasses. "Telescope crown" and "Telescope flint" are two glasses which give similar spectra, and approximate achromatism from the red to the violet.

The Society then adjourned until June 28th, when the meeting will be held, by the invitation of Professor W. G. Adams, in the laboratory of King's College.

CORRESPONDENCE.

ESTIMATION OF AMMONIA IN ITS SALTS.

To the Editor of the Chemical News.

Sir,—The following are the results of a few experiments on the estimation of ammonia in its salts which may prove of interest.

A weighed quantity of $(NH_4)_2SO_4$ was taken, dissolved in a small quantity of water, and N/5 Na_2CO_3 solution added in excess of that demanded by theory. The solution was then boiled vigorously for 10 to 15 minutes. After cooling the excess of soda was titrated with N/5 HCl solution. The difference between these two readings gave the amount of N/5 Na_2CO_3 used in the decomposition of the ammonium salt.

As will be seen by the tabulated results, the numbers obtained are concordant, and the process in rapidity and simplicity is superior to the ordinary distillation method, except when large quantities of acid are mixed with the salt, as in Kjeldahl's estimation.

Grms. Wt. of $(NH_4)_2SO_4$.	Added c.c. N/5 Na_2CO_3.	C.c. N/5 H_2SO_4.	Used c.c. N/5 Na_2CO_3.	(NH_4). P.c.
0·2	30	14·9	15·1	27·28
0·2012	20	4·9	15·1	27·12
0·1907	20	5·6	14·4	27·28
0·2	20	5	15	27·1
0·2	20	5	15	27·1
0·2	20	4·9	15·1	27·28
0·2	20	4·9	15·1	27·28
0·2	20	5	15	27·1
0·2	20	4·9	15·1	27·28

—I am, &c.,

M. Bennett Blackler.

Finsbury Technical College,
June 14, 1901.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxii., No. 21, May 28, 1901.

Hydrogenation of certain Aromatic Carbides.—Paul Sabatier and J. B. Senderens.—In a recent research, the authors found that reduced nickel has the power of directly fixing hydrogen on to a great number of organic substances. From this discovery can be deduced a general method of preparation of cyclohexane and the homologous carbides. Whilst investigating the conditions of this preparation, the authors find that below 250° hydrogenation takes place with no complications for benzene and for all its methyl derivatives which have been investigated, toluene, ortho-, meta-, and para-xylene, mesitylene, and pseudocumene. The corresponding cyclohexane is obtained as a single product in a state of great purity, often containing nothing more than a little of the primitive carbide, which is very easy to eliminate. The various products are studied individually.

Wave-lengths of certain Lines in the Iron Spectrum.—Ch. Fabry and A. Perot.—The iron spectrum is one of those which is usually taken as a comparison spectrum from which other wave-lengths are measured. It contains a great number of lines, of which many are too feeble to furnish good measurements. The author determines a certain number of these by comparison with the lines of the cadmium spectrum measured in absolute values by M. Michelson. The numbers obtained are compared with Rowland's standard wave-lengths.

Density of Alloys.—Edm. van Aubel.—An alloy of aluminium and antimony, corresponding to the formula AlSb, has for its fusing-point 1078—1080°, whilst aluminium and antimony melt respectively at 660° and 630°. The author examines this curious alloy to find whether any change in volume occurs during its formation. Determinations of its specific gravity were made with the hydrostatic balance. The mean of results obtained give as the density of the alloy, compared with water at 4° and in a vacuum, the value 4·2176. If no variation in volume took place, the alloy should have a density 5·2246, taking for aluminium and antimony respectively the values 2·67 and 6·72. The observed density is therefore considerably less than the theoretical density, and shows that, during the formation of this alloy, a considerable increase in volume takes place, such a result forming an exception to Matthiessen's rule; this can be expressed by saying that 7·07 c.c. of aluminium + 12·07 c.c. of antimony give rise to 23·71 c.c. of the alloy AlSb.

The Reduction of Silver Chloride by means of Hydrogen, and the Inverse Reaction.—M. Jouniaux.—When sealed tubes containing finely-divided silver and dry hydrochloric acid, or silver chloride and pure hydrogen, are heated for progressively increasing times, the quantity of hydrochloric acid contained in the gaseous mixture tends towards a fixed limit depending on the temperature of the experiment. Above 600°, a common limit is arrived at for the two systems. According to M. Berthelot's determinations, the reduction of silver chloride by hydrogen is accompanied, at a temperature of 15° C., by an absorption of heat of 7000 calories. If it is admitted that this reduction is still endothermic at the temperature of the above experiments, the law of the displacement of the equilibrium by variations of temperature is found to be verified. In the second place, the author examines the influence which internal pressure exerts on the formation of hydrochloric acid.

Action of Mercuric Oxide on Aqueous Solutions of Metallic Salts.—A. Mailhe.—In 1859, H. Rose stated that mercuric oxide displaced the strong bases from solutions of their chlorides, but could not replace the solutions of their oxygen salts. The author makes a fresh investigation of this subject, and obtains very different results from those obtained by Rose. When oxide of mercury acts on zinc chloride, an oxychloride of zinc is produced of formula $ZnCl_2.3ZnO.3H_2O$. Nickel chloride is completely precipitated by mercury oxide in the state of oxide, a green oxychloride being formed of formula $HgCl_2.NiCl_2,7NiO10H_2O$. Experiments were also tried with cobalt and copper salts.

Central Technical College Old Students' Association.—The Fourth Annual Dinner of the Association of Old Students of the Central Technical College will be held at the Restaurant Frascati, Oxford Street, on Wednesday, July 3rd, at 7.30 p.m. Professor O. Henrici, F.R.S., President of the Association, will take the chair. Tickets (price 6s.) can be obtained on application to the Hon. Secretary, Mr. Maurice Solomon, 12, Edith Road, West Kensington.

Association of the German Chemical Industry.—The annual meeting of this Association will be held at the Patriotic Building, Hamburg, on September 21st and 22nd. Dr. J. F. Holtz is to preside.

MEETINGS FOR THE WEEK.

FRIDAY, 28th.—Physical, 5 (in the Wheatstone Laboratory, King's College). "The Effect of a High Frequency Oscillatory Field on Electrical Resistance," by S. A. F. White. "The Spectrum of Cyanogen," by E. C. C. Baly and Dr. H. W. Syers.

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PHYSICS .. .. A. GRIFFITHS, D.Sc.
METALLURGY.. G. PATCHIN, A.R.S.M.

A Course of EIGHT LECTURES on the "HISTORY OF CHEMISTRY" will be given by Dr. J. E. MACKENZIE on FRIDAY EVENINGS, at 8.30, commencing on MAY 31.

Prospectuses on application to Secretary.

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MICHAELMAS TERM.—Monday, October 7, to Saturday, December 14.
LENT TERM.—Monday, January 6, to Saturday, March 22.
EASTER TERM.—Monday, April 14, to Saturday, July 26.

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THE CHEMICAL NEWS.

Vol. LXXXIII., No. 2170.

THE CIRCULATION OF SALT AND GEOLOGICAL TIME.

By J. JOLY, Sc.D., F.R.S.

Very full information relating to the chlorine content of rain water falling in various parts of the British Isles is on record. What is wanted is fuller knowledge of the chemical character of rains falling in inland areas, more especially as to their content of sodium. The broad fact at our disposal is that as we proceed inland a rapid diminution of the percentage of chlorine appears. In inhabited parts of Europe, but 200 miles from the sea, the proportion observed appears to be one-twelfth, normally, of what is observed 30 or 40 miles from the sea. In India, about 300 miles from the sea, it was found to be 0·04 per 100,000.

In inland countries it is extremely doubtful, according to our present knowledge, if *any* of the chlorine observed in rain is derived from the sea, for the circulation of salt from the earth to the air or from inland salt deposits, along with other mineral dust, may be accepted as *inevitable*. Raised with every wind, again washed down with rains, evaporated to dryness, and again raised mingled with the light dust of soils, an amount of saline matter comparable with so minute a quantity of chlorine as was observed in India might well circulate from the earth to the air, and be returned by the rains to the rivers. Such salt is, of course, derived by solvent denudation from the soils.

In a country like ours where no point is more than a few score of miles from the sea, coastal conditions prevail over its entire area. Even within the small British area, however, there appears to be a rapid diminution in the proportion of chlorine carried by winds to the more inland parts. This is observed even in the more inhabited districts, notwithstanding the fact, pointed out by Dr. Angus Smith, that where coal is being consumed on a considerable scale this proportion must be expected to rise. Although this is so I do not think it can be doubted that a large part of the chlorine of British rivers, and of well waters also, must be sea derived. A simple comparison of the chlorine content of British surface waters and of rain, bearing in mind the inevitable concentration of the latter by evaporation, sufficiently demonstrates this fact. This is pointed out in my paper, "An Estimate of the Geological Age of the Earth" (p. 35). As no one appears to have disputed the point (so far as I am aware), it is needless to refer to it further.

That some of the salt lakes of the earth derive something from wind-born sea salts is very certain. Calculations similar to Mr. Ackroyd's regarding the amounts annually derivable from rain by soils are on record, and have been applied to agricultural considerations; as by Pierre in France ("Air and Rain," p. 233). The whole facts of the case entirely negative the wide deductions which Mr. Ackroyd would place upon such calculations. The very variable composition of salt lakes must be regarded surely as an insuperable objection to his views! The Dead Sea, for instance, shows a very large excess of magnesium salts over sodium salts; the chlorides constituting 15·9 per cent and 3·6 per cent respectively of the total solids. There is even a large excess of calcium over sodium in its waters. In the Great Salt Lake the proportions are just the other way; the percentages are nearly marine; 11·9 of sodium chloride and very little magnesium chloride, but 1·1 per cent. There is relatively very little calcium. Now this is the more embarrassing for Mr. Ackroyd's hypothesis in that the first lake is close to the sea, the latter very remote from it. Thus, the lake which is most favourably situated for the rain supply of sea-salts is just that one which most completely departs in its chemical composition from that of the ocean. Again, we find a lake, such as the Elton Lake of the Kirghis Steppe, 200 miles from the Caspian, possessing a chemical composition approximating to that of the Dead Sea: 19·7 per cent of $MgCl_2$, 5·3 per cent of $MgSO_4$, and 3·8 per cent NaCl. Calcium is, however, in its case absent or inappreciable. Mr. Ackroyd appears to be aware of this difficulty, and would restrict attention to the chlorine and bromine ions. But this will not get over the difficulty; for how did these ions get in without bringing their attached metals along with them? Elsewhere throughout his paper Mr. Ackroyd assumes that the chlorine in rain goes about with its full complement of sodium.

It would appear, then, that in order to support Mr. Ackroyd's views we must assume that magnesium and sodium rains are distributed irregularly over the earth and persistently frequent certain localities! Now while the observed wide differences in chemical composition are entirely at variance with a pluvial origin, the rain being supposed to derive its burden from the common reservoir of the ocean (almost homogeneous in composition), they are quite in accord with an origin by solvent denudation, as a glance at the considerable differences of river analyses will show, and as indeed would be *a priori* inferred from the wide range of solubility and chemical composition of the surface materials of the earth.

Mr. Ackroyd's conclusions as to the age of the earth appear based on the following reasoning:—The chlorine content of the Aire as derived from its limestone bed is about 0·2 per cent of what it gets from rain in a region in which he has proved that all, or nearly all, the chlorine is derived from rain. This measures the rate of solvent denudation generally, and in rivers generally there will be a similarly small proportion between "earth-salts" and "sea salts." This is an argument *a particulari ad universale* with a vengeance. It is really bewildering! What about the other salts in solution not chlorides? Mr. Ackroyd's figures are $CaCO_3$, 10 grains per gallon; Cl in "earth-salt," 0·001; Cl in "sea-salt," 0·699. The two latter figures *alone* are "to be taken into account in ascertaining the rate of solvent denudation now in progress." But are they? Are not the 10 grains of calcium carbonate treated with unjustifiable neglect? Suppose the river originated in a granitic or basaltic district, surely this $CaCO_3$ would be represented by solids in solution, such as alumina, oxides of iron, sulphates of sodium and potassium, carbonate of magnesia, silica, &c.! Why neglect the sodium herein contained because it is in excess of the sodium equivalent of the chlorine present? But this is precisely what Mr. Ackroyd has done in his "solution of the problem." That this is indeed so will appear in a simple demonstration of the *limit* of the error to which the incompleteness of our knowledge as to the part played by rain-salts can lead in deducing the age of the earth from the rate of solvent denudation of sodium. Such a demonstration will at once serve to show the illegitimacy of Mr. Ackroyd's conclusions, and will serve as a reply more complete than can be attempted in letters to correspondents who, not fully going into the matter, have written to me on the circulation of sodium as affecting the estimate of geological time.

Professor Dittmar in his report on the chemical composition of the ocean shows that *the amount of chlorine present is in excess of the sodium*, so that, attaching chlorine ions to sodium ions, there remains over a large excess of chlorine; appearing in the statement of total solids as 10·8 per cent of $MgCl_2$. We have, in fact, 77·7 per cent of NaCl and 10·8 per cent of $MgCl_2$. A simple calculation will show that it results that 18 per cent of the Cl must be otherwise allocated than to the sodium, or is, in short, in excess of the Cl equivalent of the sodium present.

Now it is certainly a fair assumption that if rain receives its salts from sea spray, a similar excess of Cl ions over Na ions will obtain in rain water. Thus, we may at least assume (in deference to the current belief that the proportions of salts in rain water and sea water are not generally quite in accord), that the sodium equivalent of the chlorine found in rain water constitutes an excessive estimate of the former. Pierre's results* to which I have already referred, fully confirm this statement. He finds, in kilogrms. received per hectare per annum, quantities of sodium chloride and other chlorides, as well as of sodium sulphate, which afford 29·7 kilos. of chlorine and 17·72 kilos. of sodium. Ascribing to this amount of sodium its equivalent of chlorine we have still a balance of over 8 per cent of the chlorine.

We now turn to what we know of the chemical constitution of river salts. I take Sir J. Murray's mean analyses of 19 chief rivers of the world. Here we find the striking fact that there is *a large excess of sodium over chlorine*; or the conditions of the sea are reversed. We find, in fact, 157×10^6 tons of sodium, and 84×10^6 tons of chlorine carried to the ocean per annum, and as these elements combine in the proportions by weight of 23 : 35 it will appear that considerably the larger part of the sodium of rivers must exist otherwise combined than with chlorine were the ionising conditions removed.

Let us now go so far as to assume that *all* the chlorine in rivers is derived from rain, and that this brings into the rivers its *full equivalent* of sodium, and we can obviously calculate the maximum possible effect upon the age of the earth arising from the circulation of salt. (This can fall short of the maximum only on the assumption of a selective retention of chlorine in soils, for which I know of no evidence). In this method of treating the quantities at our disposal we leave, in short, the whole of the sodium equivalent of the chlorine of rivers out of account in deducing the age of the earth. Not to over-weight this paper with figures, I may state that the result of the new calculation is that the previous estimate of 96 millions of years rises to something under 148 millions of years. This result is, however, above the maximum deducible even on the foregoing assumptions, for as we diminish our estimate of the chlorine derived by solvent denudation during geological time we increase the estimate we necessarily make for original sodium in the ocean derived by a primeval acid denudation effected by free HCl (for we must assume so much more chlorine to have been free in the original atmosphere), and thus we are bound to diminish our numerator as well as our denominator. The final result would be 141×10^6 years. These figures are easily verified by reference to the quantities given in my paper.

The assumptions made in obtaining this upper limit are, I need scarcely point out, unjustifiable. We are not at liberty to ascribe all the chlorine of the rivers to rain. Whether derived directly from the rocks and soils, from extravasated deposits, as when combined in the ores, or from accumulations due to past or present inland denudation in "rainless" areas, this element so far as it is a carrier of sodium must enter our denominator. Nor can we assume the chlorine of rain water a fair measure of sodium transported from the sea, seeing that such chlorine if directly sea-derived should to the extent of 18 per cent exist combined with magnesium or other element, and as matter of observation does so consist to the extent of over 8 per cent. And again, what chloride of sodium is found in rain water is very surely in part derived from the land. Finally, what we know of the percentage of chlorides in inland rains points to a supply inadequate to furnish the quantities appearing in Sir J. Murray's analysis of mean river water, for of coastal rains by far the greater part finds its way back quickly and directly to the sea by the small rivers and streams (such as the Aire), and does not enter into the composition of the larger rivers, the catchment areas of which are either far inland or rise on the land side of the great mountain ranges. The amount of chlorine appearing in the mean river water is a little over 0·30 parts per 100,000. Contrast this with the estimate 0·04 obtained from rain falling 300 miles from the sea in India, or the Darmstadt estimate 0·09 part per 100,000. Both localities being still relatively close to the sea. On all these grounds I have restricted my allowance for rain-borne chloride of sodium to 10 per cent of what appears in rivers.

We might base an allowance on the scanty knowledge we possess as to the chlorine content of rains falling 200 or 300 miles from the sea. Let us accept 0·10 per 100,000 as the average amount of Cl carried by rains to the rivers after evaporation, and assume that all this was of marine origin, and brought with it its full equivalent of sodium, we thus assume that one-third the chlorine in rivers is derived from the ocean. We now calculate what correction on the 96 millions of years this will involve.

The total chlorine discharged by rivers annually into the ocean is 84×10^6 tons, and 33 per cent of this is 28×10^6 tons; this is, we assume, derived from the ocean. The sodium equivalent of this is $18{\cdot}4\times10^6$ tons. Of the total Cl discharged by rivers we see that 56×10^6 tons (the part derived from the rocks) are not cyclical. If now we assume geological time to come out at about 100×10^6 years we find that the rivers have contributed to the original ocean 5600×10^{12} tons Cl during geological time. Deducting this from the $28{,}316\times10^{12}$ tons of Cl now in the ocean we have the amount $22{,}716\times10^{12}$ as primevally free, and which on the basis of calculation given in my paper was competent to introduce 1000×10^{12} tons of sodium from the primeval rock crust if we assume it to have taken part in an acid denudation. Hence the sodium in the ocean which has to be accounted for by river supply is reduced from $15{,}627\times10^{12}$ to $14{,}627\times10^{12}$ tons. This is the numerator.

The annual river supply of sodium is to be 157×10^6 tons less $18{\cdot}4\times10^6$ carried by rain from the ocean, or 139×10^6 tons. This is the denominator. The quotient is 105×10^6. Allowing, as I have done in my paper, a deductive correction for direct coastal denudation, we may state our final result as just about 100 million of years. We are not justified in stating our result more definitely. We keep in mind that our knowledge of river analysis and of ocean mass are certainly not final.

So far then as errors from rain-born chloride of sodium can affect our result surely the limits are fixed with sufficient straitness! We have 96 millions of years if we accept the correction of 10 per cent on the chloride of sodium of rivers; we have 105 millions of years if the correction should be 33 per cent. I do not believe an unbiased consideration of the knowledge at our disposal will permit of a larger allowance.

Mr. Ackroyd's remarks as to the primeval conditions have not added anything to existing arguments which would require remark here. I have endeavoured in previous papers to show that, when an attempt is made to introduce some definiteness into the many questions raised, the vague assertions cease to be convincing. The limited duration of primeval high-temperature aqueous denudation, the very ineffective action of superheated waters on crystalline rocks (as shown by Daubrée's experiments), the obvious fact that the acid denudation cannot be supposed restricted to sodium silicates only, all are overlooked by those who prefer vague generalities to what degree of accuracy is attainable in the discussion.

Finally, Mr. Ackroyd is mistaken as to the teaching of the calculation showing that the missing sodium of the sediments is equal to, or in excess of that contained in the ocean. The greater part of these sediments, we are assured, were laid down under conditions not inimical to

* Pierre's figures for the several salts in the units mentioned above are:—

NaCl	37·5	Na_2SO_4	8·4
KCl	8·2	K_2SO_4	8·0
$MgCl_2$	2·5	$CaSO_4$	6·2
$CaCl_2$	1·8	$MgSO_4$	5·9

A rain fall of 60 c.m. per annum is assumed.

life; or, as Sir Archibald Geikie has contended for the very ancient Torridonian rocks, under physical conditions much as obtain to-day. But this is not all. The oldest sediments are just those which are chemically the least impoverished and the least washed out of the whole series, and, indeed, might almost be identified by their higher alkali percentages. This fact is obviously quite opposed to the view that they were exposed to more intense solvent actions than obtain to-day. In the light of the fact that the internal evidence—chemical, physical, and organic—afforded by the successive strata controverts the convergence of denudative activity which some have casually assumed, the calculation in question *does* oppose the theory of a sodium-charged primeval ocean. We are assured, in fact, that the introduction of sodium age by age had to wait upon the denudation of the rocks, and was thus regulated by a rate to which we know of no disturbance.

BARYTA IN SULPHATED MINERAL WATERS.

By F. CARLES.

A FEW months ago I announced before the Academy of Medicine the presence of lead, copper, baryta, lithia, fluosilicates, and fluoborates in the waters from Néris-les-Bains. As these waters contain both alkaline sulphates and alkaline bicarbonates doubt was thrown on the existence of soluble bicarbonate of baryta in the presence of alkaline sulphates. This contradiction of the law of Berthollet was first observed by us; to get a satisfactory explanation I assumed that there must be an antagonism with regard to baryta between the action of the sulphates and that of the bicarbonates.

Heat and the pressure of the carbonic acid appeared to me to cause the balance to lean in favour of the bicarbonates. However, as we do not remember ever to have shown this antagonism experimentally, the previous doubts held good.

Two months ago we learnt that there are several quarries of fluor-spar, and even one of barytine, in operation near Néris. Analysis showed that this barytine contained an appreciable amount of fluosilicates. Its identity once established we endeavoured to submit this substance to the chemico-geological treatment mentioned above, but this time with carbonic acid under considerable pressure.

For this purpose we finely triturated several grms., and boiled the material for three hours in water containing twice the amount of pure carbonate of soda. At the end of this time the solid portion consisted of undecomposed sulphate and fluosilicate of baryta and carbonate of soda in excess; and the result of the reaction was carbonate of baryta, sulphate of soda, and fluosilicate of soda. A few drops of phthalein showed by its red colour the alkalinity of the solution. It is certain that if we had then added to this mixture an acid capable of dissolving the carbonate of baryta, the sulphate of soda would have been rendered entirely insoluble.

This mass, suitably diluted with water, was placed in a Seltzer water bottle, and supersaturated with carbonic acid with the aid of "sparklets." The rose-colour immediately disappeared, and the pressure was sufficient to empty the bottle when the valve was opened. After twelve hours the liquid, passed through a filter, was of irreproachable limpidity.

The liquid was then divided into two equal parts, each portion being placed in a different kind of vessel; that is to say, one portion was placed in long narrow tubes, the other in conical Bohemian flasks with very wide bottoms. By this means one liquid had in air surface what the other had in thickness, and *vice versa*.

In both cases the liquids remained for several days exposed to the air without any change, but on the third day the one in the matras with the large air surface had commenced to become cloudy. In the long narrow tubes, on the contrary, this did not occur until about double that time.

This detail appears to us to be worth mentioning with regard to the conservation and handling of bicarbonated waters at the springs.

To hurry on the decomposition of these two liquids they were placed on the water-bath. The carbonic acid came off slowly, and at the same time a very considerable precipitate appeared. On observing this precipitate very carefully it could be plainly seen that it consisted of two bodies of different densities. As a matter of fact, analysis proved this to be the case; there was first carbonate of lime, then carbonate of baryta, and finally even traces of strontia. The bartya was in relatively considerable proportion, and sufficient to respond immediately and distinctly to the reactions with sulphate of lime, sulphate of strontia, chromate of potassium, and finally the spectroscope.

It is therefore placed beyond doubt that sulphated and bicarbonated mineral waters containing excess of carbonic acid are capable of decomposing sulphate of baryta, and of keeping bicarbonate of baryta in solution in the presence of alkaline sulphates.

It is extremely probable that the presence, in these same waters, of lead, strontium, and lime as soluble bicarbonates is caused by similar reactions.

These facts appear to have a considerable importance from the hydrological point of view. They show us that we are by no means certain of the nature of the compounds formed by metals in bicarbonated waters.

They explain to us the tolerance of the human stomach for certain mineral waters rich in sulphate of lime, which official analyses show to contain about 2 grms. per litre.

Some springs at Bagnères and in the Contrexéville district are cases in point.* It is beyond question that if they were not bicarbonated by various oxides, and if they were not united to other salts, they would act as highly selenitic waters, and would no longer be tolerated.—*Journ. de Pharm et de Chim.*, Series 6, vol. xiii., No. 12.

NOTE ON THE PREPARATION OF DIMETHYL SULPHATE.

By M. BENNETT BLACKLER.

I HAD occasion to prepare the above compound for Prof. R. Meldola, F.R.S., who desired to test that elegant method of methylation described by Ullmann and Wenner (*Ber.*, 1900, xxxiii., 2476).

At first I adopted the usual method of preparation, *i.e.*, to distil methyl alcohol with 10 parts of strong sulphuric acid. By slightly altering the conditions of experiment I obtained varying yields which were not at all satisfactory.

It seemed probable that if the reaction could be carried out in two parts the process would be more under control, and the great loss by carbonisation to some extent prevented.

The first step is to prepare methyl ether. This gas is absorbed in large quantities by strong sulphuric acid, giving a compound of the formula $SO(OH)(OCH_3)_2$ (*Ber.*, vii., 699).

When heated this compound evolves methyl ether until the temperature reaches from 150—160° C. The product obtained is soluble in water, showing absence of dimethyl sulphate, but on distilling charring takes place, and dimethyl sulphate distils over. On rapidly heating the compound, $SO(OH)(OCH_3)_2$, less methyl ether is liberated, and the yield of dimethyl sulphate is improved. The yields obtained from the last two experiments were

* The following are some of the amounts of sulphate of lime found:—Contrexéville, Martigny, Norroy, 1·59 grms. per litre; Hagecourt, 1·81; Renoncourt, 1·95; Bagnères, Salut, and Tivoli, 1·85 to 1·91.

superior to those first obtained, but there was loss of methyl ether in the process.

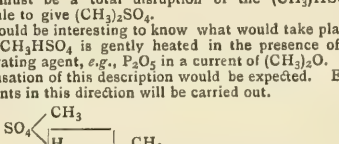
To prevent this loss I re-absorbed the ether liberated, distilled the product, and again absorbed the ether, carrying this operation out several times. The several absorptions and distillations made the process inconvenient.

As sulphuric acid containing absorbed methyl ether ceases to liberate the gas when heated above 160° C. it seemed reasonable to expect that sulphuric acid heated above 160° C. would completely absorb methyl ether. This is the case, and the product so obtained gives a comparatively large yield of the alkyl sulphate on distillation.

From the results given below it will be seen that, while the yield of sulphate has increased, the amount of sulphuric acid used has correspondingly decreased.

If the compound formed between the methyl ether and the sulphuric acid at 160° C. is the acid sulphate, then the smallness of the yield finally obtained is accounted for, as there must be a total disruption of the $(CH_3)HSO_4$ molecule to give $(CH_3)_2SO_4$.

It would be interesting to know what would take place when CH_3HSO_4 is gently heated in the presence of a dehydrating agent, *e.g.*, P_2O_5 in a current of $(CH_3)_2O$. A condensation of this description would be expected. Experiments in this direction will be carried out.



Expt.	Methyl alcohol.	Sulphuric acid to prepare $(CH_3)_2O$.	Total H_2SO_4.	Yield of $(CH_3)_2SO_4$.
	C.c.	C.c.	C.c.	Per cent.
(1).	50		221·5	2·6
(2).	100		443	9·6
(3).	50	33·2	83·2	12·3
(4).	50	33·2	83·2	15·7
(5).	200	132·8	337·8	20·1
(6).	100	66·4	166·4	21

Method.

(1). Distilled mixture, using naked flame.

(2). Heated mixture gradually on a sand-bath, then distilled, using naked flame.

(3). Prepared $(CH_3)_2O$, and passed it into 50 c.c. H_2SO_4, then slowly heated, and finally distilled.

(4). Treated same as in 3, except that the sulphuric acid solution was heated rapidly.

(5). Absorbed $(CH_3)_2O$ in 100 c.c. H_2SO_4, distilled and obtained 18 c.c. $(CH_3)_2SO_4$. Absorbed ether evolved in 50 c.c. acid; this on distillation gave 17 c.c. $(CH_3)_2SO_4$. Continued this process, and obtained 11 c.c. $(CH_3)_2SO_4$ more, using 55 c.c. H_2SO_4.

(6). Absorbed ether in 100 c.c. H_2SO_4, kept at 160° c.c. on a heated sand-bath, then distilled.

The Toxicity of Expired Air.—E. Formanek.—From the lungs of a healthy man or animal there is no toxic substance given off by the respiratory canal, as has been stated by several authors; sometimes the expired air contains traces of ammonia; this is a pathological product which only occurs in the case of dental caries or of pulmonary complaints. It is this ammonia that other writers have collected in the water of condensation of the expired air, or in sulphuric acid through which the expired air was made to pass, in every case in which the products of expiration were found to be toxic. It is not the fact that this toxicity was due to a normal, constant alkaloid, the presence of which has never been established, and which the careful experiments of M. Formanek have shown to be non-existent.—*Archiv. f. Hygiene*, vol. xxxviii., p. 1.

ON THE MELTING-POINT OF GOLD.*

By LUDWIG HOLBORN and ARTHUR L. DAY.

In connection with the measurement of high temperatures with the gas thermometer (Holborn and Day, *Am. Journ. Sci.*, 1900, [4], x., p. 171), the melting-points of various metals lying between the temperatures 300° and 1100° were determined. The two methods employed were distinguished by the names "wire method" and "crucible method." The wire method consisted in inserting into the hot junction of the thermo-element about 1 c.m. of the wire whose melting-point was to be determined, and observing the E.M.F. at the moment of melting and consequent interruption of the circuit; the crucible method, on the other hand, involved the introduction of a thermo-element, properly protected by porcelain tubes, into a comparatively large mass of the metal. The melting-point of gold was determined at that time by the wire method only.

On account of the special importance which has been attached to the melting-point of gold for comparing the temperature scales of various observers, it seemed to us advisable to make a further determination of this melting-point by the crucible method as well, and at the same time to investigate whether the surrounding atmosphere exerts any influence on the melting temperature.

For this experiment some 450 grs. of pure gold were used, the purity being vouched for by the Gold- und Silber-Scheideanstalt at Frankfort-on-Main, where it was obtained. For the sake of certainty, however, a sample weighing 2 grs. was also analysed in the chemical laboratory of the Reichsanstalt, but no impurities were found.

The gold was melted in the same oven which was described in the former paper, and measured with the same thermo-element which had served for the observations by the wire method.

Preliminary trials made with a smaller quantity of the metal (350 grs.) in a thin porcelain crucible yielded ill-defined "time curves" on account of the small latent heat of fusion, and also a difference between the melting and solidifying temperatures amounting to as much as 4°. Afterward, using 450 grms. of gold and placing the light crucible in a larger one lined with asbestos, the distribution of heat was more even, and excellent results were obtained. Crucibles of mixed graphite and clay, with walls 5 m.m. in thickness, also yielded satisfactory results—in fact, we afterwards restricted ourselves to these crucibles entirely, using old ones from which the graphite had been burned away where the reducing action was not needed.

The gold was melted under two different conditions, either in the reducing atmosphere of a graphite crucible, carbonic acid gas being also sometimes introduced, or in a double porcelain or thick clay crucible (graphite and clay from which the graphite had been burned away), in the presence of atmospheric air, and later in an atmosphere of oxygen. The gas was introduced into the molten metal through a thin porcelain tube, as described in the experiments with silver (previous paper, *loc. cit.*). Under these two conditions, both melting- and solidifying-points were observed.

Table I. contains the temperature, t (in microvolts and degrees), of the observed solidifying-points, F, and melting-points, M. Under t is contained the number of ampères carried by the oven coil during the observations.

The various stages of t show no systematic differences, and the final mean is 1063·5°.

The forms of the time-curves, some of which are given in Table II., vary somewhat under the different conditions; the measurements in the oxygen atmosphere being especially conspicuous in this particular.

* Communication from the Physikalisch-Technische Reichsanstalt, Charlottenberg, Germany. From the *American Journal of Science*, Series 4, vol. xi., No. 62.

TABLE I.

Date.		t.		t: MV.	t: Degrees.	Mean.
Graphite Crucible.						
June 21..	..	8·0	F	10194	1063·3	
		9·2	M	10197	1063·6	
		7·5	F	10194	1063·3	
		8·8	M	10197	1063·6	1063·5°
July 9 ..	..	6·8	F	10197	1063·6	
		8·3	M	10196	1063·5	
		6·8	F	10197	1063·6	
		8·2	M	10195	1063·4	
Graphite Crucible. Atmosphere of CO_2.						
July 11 ..	..	7·2	F	10198	1063·6	
		8·5	M	10198	1063·6	
		7·0	F	10196	1063·5	1063·5°
		8·2	M	10199	1063·7	
		6·8	F	10194	1063·3	
		7·9	M	10196	1063·5	
Double Porcelain Crucible.						
June 27..	..	8·0	F	10190	1063·0	
		9·0	M	10198	1063·6	1063·3°
		7·5	F	10188	1062·8	
		9·5	M	10197	1063·6	
Double Porcelain (or Clay) Crucible. Oxygen Atmosphere.						
June 29..	..	7·3	F	10200	1063·8	
		8·7	M	10199	1063·7	
		7·0	F	10192	1063·1	
		8·5	M	10199	1063·7	
July 12 ..	..	6·7	F	10189	1062·9	1063·5°
		7·8	M	10195	1063·4	
		6·5	F	10193	1063·2	
July 13 ..	..	6·2	F	10198	1063·6	
		7·5	M	10203	1064·1	

TABLE II.

"*Time Curves*" (MV).

	Gold in graphite.		Gold in graphite. Atmosphere of CO_2.		Gold. Atmosphere of O.		Copper in air.
Mins.	F.	M.	F.	M.	F.	M.	F.
1	10331	10084	10402	10117	10366	10027	10590
2	10261	10150	10346	10166	10276	10074	10470
3	10209	10190	10298	10192	10223	10101	10352
4	10207	10194	10246	10195	10205	10144	10281
5	10203	10195	10200	10197	10201	10170	10217
6	10200	10195	10199	10194	10199	10198	10204
7	10199	10195	10199	10194	10199	10254	10212
8	10198	10195	10199	10194	10198	10238	10212
9	10197	10197	10198	10194	10196	10222	10212
10	10197	10199	10198	10196	10193	10205	10212
11	10197	10203	10198	10196	10194	10202	10212
12	10196	10212	10198	10197	10193	10201	10212
13	10196	10222	10198	10198	10194	10202	10212
14	10195	10231	10198	10199	10192	10203	10212
15	10194	10240	10197	10200	10191	10203	10212
16	10192	10248	10198	10201	10189	10203	10212
17	10188	10257	10197	10202	10186	10208	10211
18	10178	10272	10197	10205	10184	10216	10210
19	10070	10400	10197	10206	10184	10212	10208
20	9995	—	10196	10205	10183	10222	10204
21	—	—	10196	10209	10174	10230	10195
22	—	—	10195	10204	10159	10360	10176
23	—	—	10195	10202	10065	—	10027
24	—	—	10194	10214	—	—	—
25	—	—	10192	10296	—	—	—
26	—	—	10190	10400	—	—	—
27	—	—	10186	—	—	—	—
28	—	—	10177	—	—	—	—
29	—	—	10053	—	—	—	—

The stationary temperature characteristic of the change of state is less well defined in this case, the temperature in observations of the melting-point often rising uninterruptedly to a point somewhat above the melting-point and coming back to it again afterward. The stirring produced by the gas bubbling through the molten metal is not the cause of this phenomenon, for the cases where carbonic acid was introduced under like conditions do not show it.

Furthermore, where the oxygen atmosphere was introduced, the time curves are always irregular and often even with ordinary air. This suggests the possibility that, in these cases, the melting metal takes on some oxygen. The effect of this irregularity upon the melting temperature, however, is small, and scarcely exceeds the errors of observation.

From the same gold which had served for the measurements in the crucible, several grms. were afterward drawn out into thin wire, 0·25 m.m. in diameter, and used for a series of control observations by the wire method, which it would be so desirable to be able to use in the case of gold. The same thermo-element was used for these also, and great care was taken that the two wires of the element enclosing the short gold wire be as free from strain as possible, to avoid rupturing the gold before its proper melting point.

Five observations yielded the following values for the melting temperature:—

September 26	.. ..	10206 MV.	1064·3°
		10197	1063·6
		10203	1064·1
		10199	1063·7
		10198	1063·6

The mean value, 1063·9°, differs only 0·4° from that obtained by the crucible method, and only 0·1° from the earlier results obtained under the same conditions (see former paper, p. 190) in which other gold was used.

For the calibration of the thermo-elements, then, the determination of the melting-point of gold by the wire method is perfectly trustworthy, and only about 0·03 gr. of gold are necessary for the determination.

If for any reason, however, the crucible method be preferred, the neighbouring melting-point of copper in air is well adapted for calibrations; our determination of it was 1064·9. This point, aside from the diminished expense, is more convenient to determine than the gold melting-point by the crucible method, on account of the greater latent heat of copper.

Table II. contains a time-curve for comparison with the gold, which was observed on October 1 with 370 grs. of copper in a thin porcelain crucible. The current strength, i, in the heating coil amounted to 5·2 ampères, and was smaller than in any experiment made with gold.

Society of Arts.—The Council have awarded the Society's Silver Medal to the following readers of papers during the Session 1900—1901:—Major Ronald Ross, F.R.S., for his paper on "Malaria and Mosquitoes"; Dr. W. Schlich, C.I.E., F.R.S., for "The Outlook for the World's Timber Supply"; Lieutenant Arthur Trevor Dawson, late R.N., for "Modern Artillery"; Fritz B. Behr, for "The Proposed High-Speed Electrical 'Monorail' between Liverpool and Manchester"; Percy R. Macquoid, for "Evolution of Form in English Silver Plate"; Professor Raphael Meldola, F.R.S., for "The Synthesis of Indigo"; Sir Joseph Fitch, LL.D., for "School Work in Relation to Business"; Gugliemo Marconi, for "Syntonic Wireless Telegraphy"; Henry John Tozer, M.A., for "The Growth and Trend of Indian Trade—A Forty Years' Survey"; Colonel Sir Thomas Hungerford Holdich, R.E., K.C.I.E., C.B., for "The Greek Retreat from India"; John David Rees, C.I.E., for "Madras, the Southern Satrapy"; the Hon. Sir John Alexander Cockburn, K.C.M.G., for "The Commonwealth of Australia"; Lieutenant Carlyon W. Bellairs, R.N., for "The Coal Problem: Its Relations to the Empire"; William Burton, F.C.S., for "Recent Advances in Pottery Decoration"; and Hugh Stannus, F.R.I.B.A., for "Some Examples of Romanesque Architecture in North Italy."

METHOD FOR PREPARING STRICTLY TENTH-NORMAL, FIFTH-NORMAL, &c., HYDROCHLORIC OR NITRIC ACID.*

By RICHARD K. MEADE.

In a paper before the Lehigh Valley Section of the Society (*Journ. Amer. Chem. Soc.*, xxiii., 12), the writer described a method for preparing strictly normal, seminormal, decinormal, &c., sulphuric acid by decomposing copper sulphate with the electric current. Since the publication of this paper, the following method, depending primarily upon the same reaction, has been tried, and found successful, for preparing one-fifth and one-tenth normal hydrochloric and nitric acid.

The method of procedure in making tenth-normal hydrochloric acid is as follows:—

12·487 grms. of pure crystallised copper sulphate are dissolved in 500 c.c. of distilled water in a lipped beaker capable of holding about a litre. Into this solution, after cooling if necessary, is introduced a cylinder of copper-foil attached to the negative wire of an electric circuit, and a platinum rod attached to the positive wire. Both the cylinder and rod should reach to the bottom of the beaker. The copper cylinder is made from copper-foil. The writer used foil 0·015 inch thick and 3 inches wide. The foil is cut the required length, which will be about three times the diameter of the beaker plus ½ inch for a lap. The foil is curled so that the ends lap. Holes are punched through the two thickness of foil with a sharp nail, and wire run through these so as to fasten the two ends together. The beaker is covered with a watch-glass perforated to allow the rod to enter, and a current of from one to one and a half ampères passed through the solution for from six to eight hours, or all night if the decomposition is begun in the afternoon. At the expiration of this time, the watch-glass is removed, and rinsed off together with the cylinder and rod into the beaker. The solution is then transferred to a litre-graduated flask, and any copper that may have dropped off the cylinder into the beaker is well washed by decantation, rinsing the beaker at the same time into the flask. Now weigh, accurately, exactly 12·215 grms. of crystallised barium chloride into a small beaker, dissolve in water, and pour into the flask. Dilute the latter to the mark, add 2·6 c.c. of water, and mix well. Allow the precipitate to settle, syphon off the clear liquid through a dry tube, upon a dry filter and funnel, and catch the filtrate in a dry beaker or stock-bottle.

The method depends upon the decomposition of the copper sulphate solution by the electric current into copper and sulphuric acid. Upon adding barium chloride to this latter, double decomposition takes place, and barium sulphate and hydrochloric acid are formed. The addition of the 2·6 c.c. of water after the solution has been made up to the mark, is to correct for the volume of water displaced by the precipitate.

In preparing tenth-normal nitric acid by this method, the only change that is made is in the substitution of 13·076 grms. of barium nitrate for the barium chloride. The quantity of copper sulphate, of course, remains the same.

In preparing large quantities of the acid it would probably be simpler to pour the solution into a stock-bottle, provided with a syphon, immediately after adding the barium chloride or nitrate, making up to the proper volume, and mixing. The solution can then be drawn off for use as wanted, after the precipitate has settled. The syphon tube must not reach so near the bottom of the bottle as to stir up the precipitate. Graduated flasks as large as two litres are carried in stock by dealers in such ware. When it is desirable to make up larger quantities of acid, ungraduated flasks can be purchased, holding as much as 10 or 12 litres. Their exact volume to any point on the neck can be found either by weighing water into them if a sufficiently large delicate balance is at hand or even by measuring water into them; the proper amounts of copper sulphate and barium chloride or nitrate can then be calculated and used to make this volume. In calibrating the flask by measuring water into it, it must be borne in mind that the ordinary flask is graduated to hold, not to deliver, the given volume. To find the volume a given flask will deliver, weigh into it say 100 grms. of water from a weighing-bottle, revolve the flask so as to wet the sides, then pour the water back, and drain the flask into the weighing-bottle for one minute. The loss in weight, on again weighing the water, may be taken as the correction to be subtracted from the volume which the flask is graduated to contain for the volume it will deliver. This method will be sufficiently accurate for the present purpose.

I have prepared only tenth-normal and fifth-normal acids by this method. Probably normal acid could also be prepared, though the waste, due to the solution retained in the precipitate, would of course, be greater owing to the larger volume of the latter.

In the first attempts to prepare tenth-normal acid by this method the barium chloride was added to the solution after the cylinder and rod had been removed, and before making up to the litre. The solution was then filtered into the graduated flask after the precipitate had settled, and the latter brought upon the paper and washed with hot water until the mark on the neck of the flask was reached. The solution was then cooled and made up to the litre. The solution, on testing, however, proved to be a little below the desired strength, due no doubt to the "holding back" of some of the acid by the precipitate. The method first given was then tried, and gave a solution of the exact strength desired with much less labour and in much less time.

Both the nitric and hydrochloric acid solutions were tested as follows:—

Fifty c.c. of the acid were made alkaline with ammonia, heated to boiling, and ammonium oxalate added. No precipitate formed in any case.

Fifty c.c. were heated to boiling, and barium chloride added. Only a very slight cloud formed. The precipitate was allowed to stand over night in a warm place, filtered, washed, ignited, and weighed. The results on the five solutions were as follows:—

No.	Solution.	$BaSO_4$ in 50 c.c. Grm.	H_2SO_4 in 50 c.c. Grm.	H_2SO_4 in 1 litre. Grm.
1.	0·1 N HCl	0·0004	0·00017	0·0034
2.	0·1 N HCl	0·0008	0·00034	0·0068
3.	0·2 N HCl	0·0030	0·00126	0·0252
4.	0·1 N HNO_3	0·0025	0·00105	0·0210
5.	0·2 N HNO_3	0·0038	0·00160	0·0320

Where the standard hydrochloric acid is intended for use in determining the alkaline earths, it would, of course, be

No.	Solution.	Standard acid taken for the test. C.c.	Standard sodium hydroxide required. C.c.	Equivalent volume of 0·10 N NaOH.* C.c.
1.	0·1 N HCl ..	10·0	10·2	10·01
		10·0	10·2	10·01
		10·0	10·2	10·01
		20·0	20·4	20·02
2.	0·1 N HCl ..	10·0	10·2	10·01
		10·0	10·2	10·01
		20·0	20·4	20·02
3.	0·2 N HCl ..	10·0	20·4	20·02
		10·0	20·35	19·97
		20·0	40·75	40·00
4.	0·1 N HNO_3	10·0	10·2	10·01
		10·0	10·2	10·01
		20·0	20·4	20·02
5.	0·2 N HNO_3	10·0	20·4	20·02
		10·0	20·4	20·02
		20·0	40·7	39·94
		20·0	40·75	40·00

* Factor for converting standard sodium hydroxide to 0·1 N NaOH=0·9813.

* Contribution from the Chemical Laboratory of Lafayette College. From the *Journal of the American Chemical Society*, xxiii., No. 5.

necessary to add a little in excess of 12·215 grms. of barium chloride, the theoretical quantity necessary to convert the sulphuric acid to tenth-normal hydrochloric acid. Indeed it would, perhaps, be better in all cases to add a slight excess of the salt since a trace of it in the solution can certainly, in most cases, do no harm.

When checked against nearly tenth-normal sodium hydroxide solution (which had been prepared from metallic sodium, carefully standardised, and kept free from carbon dioxide), using phenol-phthalein as an indicator, the results showed each solution prepared to be of exact strength, as shown by the accompanying table.

A BIBLIOGRAPHY OF STEEL WORKS ANALYSIS.

PART IX.

By HARRY BREARLEY.

(Continued from p. 292).

PHOSPHORUS.

II. GRAVIMETRIC ESTIMATIONS (*continued*).

II.*b*. *Precipitating Finally with Magnesia.*—

1280. CHAMPION and PELLET (*C. N.*, xxxv., 115).—Weighing as $Mg_2P_2O_7$ is less suited for estimating small amounts than direct weighing of the PMo.

1281. KERN (*C. N.*, xxxv., 1).—Dissolve in aqua regia rather than HNO_3, in order to destroy organic matter, which otherwise interferes with the precipitation as PMo. Dissolve PMo in AmHO and add Mg.

1282. STOECKMANN (*C. N.*, xxxvi., 275).—The evaporated solution of the spiegel is heated to destroy organic matter, PMo formed in HNO_3 solution at 30°, and P re-precipitated with Mg.

1283. FRICKE (*J. I. S. I.*, 1881, 283).—Dissolve in HNO_3, ignite dried residue to destroy C, and make Mo-Mg precipitation.

1284. PARNELL (*C. N.*, xxiii., 145) and FOERSTER (*C. N.*, lxvii., 241).—If both solutions are heated before mixing, the $Mg_2P_2O_7$ is free from impurity. A correction for bulk of liquid is necessary.

1285. OGILVIE (*C. N.*, xxv., 277).—0·3 grm. P_2O_5 may be completely precipitated with Mo. Uses 40 MoO_3 to 1 P_2O_5. Precipitate finally with Mg.

1286. GILBERT (*C. N.*, xxviii., 225).—Mg mixture should be made up without sulphate, otherwise MgO is precipitated. Uranic titration of P_2O_5.

1287. ATKINSON (*C. N.*, xxxv., 127).—Silicates introduce positive errors into the Mo-Mg estimation.

1288. AGTHE (*C. N.*, xlv., 284).—Complicated Mo-Mg process. The solution should be cooled to ordinary temperature before the PMo is filtered off.

1289. STUNKEL (*C. N.*, xlvi., 66).—Form PMo in presence of 15 per cent $AmNO_3$, dissolve in AmHO, and add Mg drop by drop. Filter after two hours' standing.

1290. WEISSMANN (*J. I. S. I.*, 1890, i., 370).—Oxidise nitric acid solution with $KMnO_4$, reduce excess with H_2O_2, and precipitate as usual.

1291. BAMBER (*J. I. S. I.*, 1894, 319).—Add Na_2CO_3 to HNO_3 solution of the iron short of alkalinity, evaporated residue leached with Na_2CO_3, and filtrate precipitated with Mg. All the As is precipitated also.

1292. ROODE (*J. C. S.*, lxviii., ii., 414).—The results are more exact when a known amount of Na_3PO_4 is added and finally deducted.

1293. RUNYAN and WILEY (*J. C. S.*, lxx., ii., 126).—The same remark applies to the citrate process.

1294. WDOWISZEWSKI (*J. I. S. I.*, 1897, ii., 502).—Mo-Mg process. Five minutes' shaking completes the Mg precipitation.

1295. GLADDING (*C. N.*, xlvi., 213).—Precipitation with Mg in neutral, faintly alkaline, and strongly alkaline solutions; the addition of Mg mixture in drops, &c.

1296. MYHLERTZ (*J. S. C. I.*, 1894, 67).—The turbidity sometimes seen on dissolving PMo in AmHO is due to ferric phosphate, and is prevented by dissolving in alkaline citrate solutions.

1297. WAKEMANN (*J. C. S.*, liv., 1131).—The Mg precipitate may be washed with advantage by dilute AmHO containing alcohol.

1298. GLADDING (*C. N.*, xlvii., 71).—The correction for solubility of Mg precipitate in mother-liquor and wash-water is practically nil.

1299. SCHMŒGER (*J. C. S.*, lxxiv., ii., 455).—The Mg precipitate need not be ignited apart from the paper if that loosely adhering is shaken into the crucible.

1300. PEITZOCH, &c. (*C. N.*, xliii., 7).—Mg added gradually, and precipitate ignited strongly in order to volatilise any adherent MoO_3.

1301. BROCKMANN (*C. N.*, xlvii., 84).—Dissolve the Mg precipitate with HNO_3 into a weighed crucible, evaporate, and ignite.

1302. NEUBAUER (*J. C. S.*, lxx., ii., 73).—The lid of the crucible is coated with MgO, in order to retain P_2O_5, which is volatilised on ignition. For a "decomposition formula" wherewith to correct results see Meinecke, *J. I. S. I.*, 1896, i., 541. Chlorides do not interfere with the Mo precipitation.

1303. LINDO (*C. N.*, xlviii., 217, 230, and 239).—Investigates precipitation with Mg, influence of heat, excess Mg, mode of adding Mg, concentration, alkalinity, solvent action of chlorides, oxalates, citrates, &c., &c.,

1304. LASNE (*C. N.*, lxxvi., 268).—Mg precipitation. Influence of time, mechanical shaking, dilution, and lime. Is the ignited precipitate $Mg_2P_2O_7$? The presence of citric acid is necessary always. *C. N.*, lxxviii., 166.—The precipitate is completely insoluble in a solution containing one-third its volume of AmHO.

1305. NEUBAUER (*J. I. S. I.*, 1892, ii., 513; and 1893, ii., 529).—P_2O_5 is lost on heating when the precipitate is formed in solutions containing too much ammonia.

1306. NEUBAUER (*C. N.*, lxx., 213).—Influence of AmHO salts, excess Mg, and alkalinity on the composition of the precipitate. Ignite precipitate white at low temperature, then blast.

1307. KENNEPOHL (*J. I. S. I.*, 1888, i., 385).—Basic slag contains but little Fe phosphide. Decompose with HCl and make Mo-Mg precipitations. Silico-molybdate is soluble in 3 per cent HNO_3.

1308. MULLER (*J. I. S. I.*, 1881, 708).—Blast-furnace slag is dissolved in HCl, evolved phosphoretted hydrogen oxidised with HNO_3 and estimated as usual.

1309. OLIVERI (*J. I. S. I.*, 1890, ii., 331).—Decompose basic slag with HCl+$KClO_3$, and estimate with Mg as usual.

1310. VOGEL (*J. C. S.*, liv., 991).—Decompose with HCl and precipitate with Mg from citrate solution.

1311. REIS (*J. C. S.*, lvi., 439).—Summarises the processes suggested for decomposing and estimating P in basic slags, and suggests modifications.

1312. SHIMER (*C. N.*, lviii., 165).—Dissolve iron in HNO_3, add $KMnO_4$, destroy excess with HCl, evaporate with H_2SO_4, and precipitate with Mo and then Mg. Works well with titanic irons. Sulphates can entirely replace nitrates in the Mo precipitation.

1313. Myhlenberg and Drown (*J. I. S. I.*, 1881, 657).—P can be completely precipitated from nitro-sulphuric filtrate of the silicon estimation (676) with Am_2MoO_4.

1314. Lindo (*C. N.*, xlix., 247).—Comparison of methods. SiO_2 should always be removed.

1315. Œttel (*J. C. S.*, lxxii., ii., 157).—Digest phosphor-bronze with HNO_3, fuse SnO_2 with KCN, boil filtrate with HCl to eliminate HCN, and precipitate with Mg. As does not interfere.

1316. Wickhorst (*J. C. S.*, lxxiv., ii., 46).—Dissolve phosphor-bronze, Cu-Sn alloys, &c., in aqua regia, add AmHO, pass H_2S, and add MgO to the filtrate.

1317. Bruyn (*J. C. S.*, lxvi, ii., 217).—Decompose phosphor-tin with Br, evaporate with HCl, electro-deposit Sn, and precipitate P with Mg.

1318. Dudley and Pease (*J. S. C. I.*, 1894, 665).—Precipitation as ferric phosphate, and then as PMo. Dissolve in AmHO, pass H_2S to remove As and Mo, and precipitate evaporated filtrate with Mg.

1319. Abel (*C. N.*, vi., 133).—Precipitate basic phosphate of iron from FeO solution, dissolve in HCl, add AmHO and H_2S, and precipitate filtrate with Mg.

1320. Spiller (*C. N.*, xiii., 170).—As 1319; but precipitates the ferric phosphate along with a little ferrous carbonate by means of Am_2CO_3.

1321. Tosh (*C. N.*, xvi., 168).—Mainly as 1320. Precipitates the P with Mg in the presence of citric acid without separating the iron. Nickles (*C. N.*, vii., 87).—Decompose Fe with Br, and, after adding AmHO, tartrate, and alcohol, precipitate with magnesia.

1322. Riley (*C. N.*, xxxvii., 68).—Dissolve in HCl, and form ferric phosphate as 1319; but precipitate finally from an AmHO solution containing 13 grms. of citric acid. Results of Mo process are low.

1323. Clymer (*J. I. S. I.*, 1888, i., 378).—Reduce to FeO with bisulphite, precipitate ferric phosphate with acetate, and make citro-magnesic precipitation. Digest $Mg_2P_2O_7$ with HNO_3, and deduct the residue from the first weighing.

1324. Scheiding (*J. C. S.*, lxviii., ii., 291).—$Mg_2P_2O_7$ obtained from citrate solution should, if black, be re-heated with $AmNO_3$.

1325. Meyer and Schmidt (*J. S. C. I.*, 1882, 372).—Perfect precipitation of the P takes place only when the citrate and AmHO are in the proportion of 1 to 2.

1326. Knap (*C. N.*, xv., 207).—In the presence of tartaric acid, P is not precipitated by Mg from an alkaline liquid if Al is also present.

1327. Glaser (*C. N.*, li., 285).—Not more citrate is used than is necessary to keep all the Ca in solution. Process used for Fe ores. *J. C. S.*, lxviii., ii., 138).—A large excess of Mg is necessary in order to form the ordinary triple phosphate.

1328. Reitmair[5] (*J. C. S.*, lx., 243).—The use of citric acid always gives imperfect results however the process is modified.

1329. Lorenz (*J. C. S.*, lxiv., ii., 185) and Kilgore (*J. C. S.*, lxviii., ii., 329).—In the absence of citric acid, MgO is always simultaneously precipitated, even when the mixture is added in drops.

1330. Tollens (*C. N.*, xlv., 209).—Moisten $Mg_2P_2O_7$ with $AgNO_3$ and heat quickly; a yellow colour indicates contamination by MgO, CaO, or their phosphates or citrates.

1331. Shutzer (*J. C. S.*, lvi., 186).—The complete precipitation from citrate solutions is assured by adding pulped filter-paper and stirring five minutes. Seyfert (*Ibid.*, 548) rubs a cropped feather against the beaker side with the same object.

1332. Ogilvie (*C. N.*, xxi., 205).—When the solution of a mineral which has not been evaporated is precipitated from citrate solutions with Mg, Fe and Al go down as silicate.

1333. Ogilvie (*C. N.*, xxxi., 274; and xxxii., 5, 12, and 70). — Investigates influence of AmHO and various salts, Fe and Al, and mixtures of these on the Mg precipitation in hot and cold solutions. Condemns the process when Fe or Al is present.

1334. Parnell (*C. N.*, xxxii., 222).—Disputes conclusions of 1333. The British Association Reports on means of estimating P_2O_5 in "commercial products" (*C. N.*, xxxii., 172; and xxxviii., 63) refer to these points and summarise work on the citric acid, magnesic, uranic, and molybdic processes.

1335. Muller (*J. I. S. I.*, 1881, 386).—Solution of basic slag at once precipitated with citro-magnesic reagent, added in drops, before making alkaline with ammonia.

1336. Edwards (*C. N.*, lxiv., 275), Von Reis (*C. N.*, lix., 107), and Jolles (*C. N.*, lxvi., 262).—Each precipitate with Mg from citrate solutions after decomposing the slag with various acids.

1337. Kalmann (*C. N.*, lv., 248).—Heat borings with CaO and $KNaCO_3$, digest with citric acid, and precipitate filtrate with Mg.

1338. Tantin (*C. N.*, xviii., 252).—Treat metal with HCl, pass gases through KHO into $AgNO_3$, decompose precipitate with aqua regia, and precipitate with Mg (see 1246).

1339. Adriaanz (*C. N.*, xxvi., 60).—As 1342; but reduce to FeO with hyposulphite, and precipitate finally with Mg. Al does not interfere.

1340. Liebrich (*J. I. S. I.*, 1895, i., 504).—To HCl solution add Am_2S, evaporate filtrate after adding Mg, ignite, re-dissolve in HCl, add AmHO, and collect the precipitated ammonium magnesium phosphate.

II.*c. Precipitating Finally in various Ways.*—

1341. Sutton (*C. N.*, i., 97 and 122).—Precipitate as phosphate of Ur and ammonia. Ca, Mg, and Ba do not interfere. Fe must be reduced to FeO.

1342. Chancel (*C. N.*, i., 230; and iii., 3).—Acid nitrate of Bi precipitates either ortho-, pyro-, or meta-phosphate from HNO_3 solutions as $BiPO_4$. Chlorides and sulphate interfere, and Fe must be reduced to FeO (with H_2S) before precipitating the P.

1343. Pisani (*C. N.*, iii., 211).—Precipitate as uranium phosphate from acetic solutions. Mg is perfectly separated. Fe and Al interfere.

1344. Birnbaum (*C. N.*, xxii., 227).—Precipitate as 1342, dissolve in HCl, add Am_2S, and estimate P in the filtrate with Ur.

1345. Munroe (*C. N.*, xxiv., 18 and 32).—To alkaline phosphate add $Al_2(SO_4)_3 + HgCl_2 + NaHO$; increased weight of ignited precipitate over that due to Al_2O_3 is P_2O_5. Or precipitate with $HgNO_3$, $Hg(NO_3)_2$, and NaHO, and ignite with CuO to retain P_2O_5.

1346. Warington (*C. N.*, xii., 209).—Describes the precipitation of P as a compound of Fe, Pb, Sn, Hg, and Ur.

1347. Kissel (*C. N.*, xx., 168).—Compares Mg, Mo-Mg, Ur, basic Fe., and Ur (volumetric) processes for estimating P. Kitchen (*C. N.*, xxvii., 199).—Contrasts the Mg and Ur processes.

1348. Ibbotson and Brearley (*C. N.*, lxxxii., 55).—The PMo formed rapidly from HNO_3 solution is dissolved in AmHO, poured into excess HCl, PbA_2 added, and, after heating, poured into a mixture of AmA and AmCl. The $PbMoO_4 \times 0{\cdot}007 = P$.

III. Volumetric Estimations.

a. Of the Molybdenum Precipitate.—

1349. Macagno (*C. N.*, xxxi., 197).—Reduce acid solution of the PMo with zinc to Mo_2O_3, and titrate with $KMnO_4$.

1350. Drown (*C. N.*, lx., 20).—Dissolve in 1·135 HNO_3 (see 677), oxidise to orthophosphate with $KMnO_4$, clear with tartaric, and titrate PMo as 1349. Silico-molybdate is soluble in dilute HNO_3. Mo_2O_3 is not easily oxidised (see 1254).

1351. Jones (*C. N.*, lxii., 220 and 231).—PMo washed with Am_2SO_4, reduced by filtering through Zn, and titrated with $KMnO_4$.

1352. Emmerton (*J. I. S. I.*, 1886, 1018).—As 1349; but filters off the zinc.

1353. Reis (*J. I. S. I.*, 1886, 390).—As 1349; or Mo-Mg process. The PMo formed in the cold is $Am_3PO_4.10MoO_3$; at 80—90°, it is $Am_3PO_4.11MoO_3$ (see 1216).

1354. Herting (*J. I. S. I.*, 1897, i., 568; 1898, i., 534).—As 1349. Reviews other rapid processes. Better to pour the Fe into the Mo solution.

1355. Schneider (*J. C. S.*, lxiv., ii., 392).—The ore is decomposed with HCl+HF, evaporated with H_2SO_4, and PMo reduced with Zn as 1352.

1356. Blair and Whitfield (*J. I. S. I.*, 1895, ii., 593).—Analyse the yellow precipitate. The solution is reduced by zinc to $Mo_{24}O_{37}$.

1357. Auchy (*J. C. S.*, lxxii., ii., 343).—Reduction to Mo_2O_3 probably; but, after filtering, it is $Mo_{12}O_{19}$.

1358. Dudley (*C. N.*, lxxvii., 195).—The reduced solution must pass into excess $KMnO_4$ without being exposed to the air, otherwise Mo_2O_3 is partly oxidised. Also Noyes and Frohman (*J. I. S. I.*, 1895, i., 505).

1359. Hundeshagen (*J. C. S.*, lxviii., ii., 85), Kilgore (*Ibid.*, 183), Cheever (*J. I. S. I.*, 1885, 737), Dudley and Pease (*J. I. S. I.*, 1893, ii., 528).—Give accounts of the zinc reduction process.

1360. Dudley, Doolittle, &c. (*J. I. S. I.*, 1894, ii., 492).—In order to obtain accurate results by titrating the reduced Mo, fixed conditions must be rigidly adhered to.

1361. Thilo (*J. I. S. I.*, 1887, i., 475).—Large PMo precipitates are not completely dried at 100°. Dissolve in AmHO, and titrate the excess, using litmus as indicator. Also Wdowiszewski (*J. I. S. I.*, 1892, i., 487).

1862. Isbert (*J. C. S.*, lii., 526; and liv., 194).—Process 1361 does not give concordant results. Suggests a method based on determining the AmHO in the precipitate. Liable (*Ibid.*).—The percentage AmHO in PMo is variable. Silico-molybdate is soluble in water, but not in $AmNO_3$.

1363. Handy (*C. N.*, lxvi., 324).—Rapid precipitation of the PMo, wash with KNO_3, dissolve in NaHO, and titrate excess with HNO_3; NaHO standardised by pure PMo; As does not interfere. (*J. C. S.*, lxvi., ii., 365).—As is eliminated by re-precipitating the PMo. Also Rothberg (*J. I. S. I.*, 1892, ii., 513).

1364. Pemberton (*C. N.*, lxix., 286).—One molecule P_2O_5 requires precisely 23 molecules Na_2O when the PMo is being neutralised. Na_2O solution freed from CO_2 by $Ba(HO)_2$. Also Day and Bryant (*C. N.*, lxx., 3).

1365. Mahon (*J. I. S. I.*, 1897, ii., 503; and 1898, ii., 557).—As 1363. P precipitated by shaking fifteen seconds; result in eight minutes.

1366. Ohly (*C. N.*, lxxvi., 200).—As 1363; or the volume of the precipitate is measured in a Gotz tube.

1367. Juptner (*C. N.*, lxxii., 172).—Measures PMo in Gotz tube. As is precipitated above 40—45° C. Borman (*J. I. S. I.*, 1890, i., 369; and Anon. (*J. I. S. I.*, 1885, 738).—Also measures the PMo in a graduated tube.

1368. Wedding (*J. I. S. I.*, 1887, 466).—Precipitates PMo without oxidising the organic matter when the carbon is low, and measures it in a tube.

1369. Reinhardt (*J. I. S. I.*, 1891, ii., 324).—Personal errors figure largely when P is estimated by measuring PMo in a graduated tube.

1370. Pemberton (*C. N.*, xlvi., 4).—Add aqueous Am_2MoO_4 to HNO_3 solution of P_2O_5; the operation is at an end when no further PMo is formed; precipitate of constant composition. Observes the interference of many inpurities. Not suitable for irons.

1371. Caldwell (*C. N.*, xlviii., 61).—Apparatus for noting the end-reaction in 1370.

1372. Grete (*C. N.*, lx., 310).—Similar to 1370; but adds a solution of glue to the titrated liquid.

1373. Schindler (*C. N.*, lviii., 61).—Dissolve PMo in AmHO, precipitate with Mg, and titrate the Mo in the filtrate with PbA_2 and tannin as in 295.

1374. Galbraith (*J. I. S. I.*, 1890, i., 142).—A few decigrms. or steel are dissolved in aqua regia, and the turbidity due to PMo compared with standards in order to trace the oxidation of the P in the "basic" steel bath. See also Alessandria (*C. N.*, lxxiv., 45).*

1375. Cheever (*J. I. S. I.*, 1885, 738) and Osmond (*C. N.*, lvi., 160).—Dissolve PMo in NaHO, acidify with HCl, and add $SnCl_2$. The blue colour is proportional to the amount of P.

1376. Namias (*J. I. S. I.*, 1891, i., 435).—Wash PMo with AmCl, digest with $Na_2S_2O_3$, and compare blue colour with standards.

1377. Jolles and Neurath (*J. S. C. I.*, 1898, 493).—Colour test based on estimation of AmHO in PMo by Nessler test is unreliable; yellow colour of the KPMo can be used. Fe and SiO_2 interfere.

1378. Fairbanks (*J. C. S.*, lxxii., ii., 72).—The MoO_3 of the PMo is estimated iodometrically as in 297.

III.b. Volumetric Estimation in Various Ways.—

1379. Johnson and Jenkins (*C. N.*, xl., 39).—In the presence of Al or Fe add tartaric acid and Mg, and titrate the collected precipitate with standard acid. The precipitate is soluble in citrate solutions.

1380. Schlickum (*C. N.*, xlvii., 106), Segalle (*J. C. S.*, lxviii., ii., 184), Gluckman (*Ibid.*, 329), Hebebrand (*J. S. C. I.*, 1898, 607), and many others.—Add standard AmHO and $MgSO_4$ to neutral solution of P_2O_5, and titrate the excess of AmHO in the filtrate.

1381. Bongartz (*C. N.*, li., 123), Emmerling (*J. C. S.*, l., 741), Kelmann and Meissels (*C. N.*, lxxii., 28), Littmann (*C. N.*, lxxx., 178), and others.—The titration of P_2O_5 in the presence of Ca, Mg, Fe, Al. &c., is made by noting the KHO used between the yellow colour of the methyl-orange and the reddening of phenolphthalein.

1382. Linossier (*J. C. S.*, lvi., 308).—Precipitate with bismuth nitrate, decompose with H_2S, filter, and titrate P_2O_5 with soda and Porrier's orange.

1383. Kratschmer (*C. N.*, xlvii., 83).—Add $AgNO_3$, filter off Ag_3PO_4, and estimate the excess of Ag. This is Perrot's process.

1384. White (*C. N.*, lvii., 187).—To sulphuric solution add $AgNO_3$ and $CaCO_3$, and titrate excess $AgNO_3$ in the filtrate.

1385. Hollemann (*C. N.*, lxxi., 102) and Clark (*J. S. C. I.*, 1888, 311).—As 1383. The Ag in

* In practice the P is determined by hammering a spoon test down to a fixed size and observing the fracture. In this way the P may be estimated to a few hundredths of 1 per cent (see Windsor Richards, *J. I. S. I.*, 1890, i., 150).

the filtrate or precipitate being estimated with KCNS.

1386. Schwarz (*C. N.*, viii., 207).—To acetic solution add PbA_2, filter, and estimate excess of Pb with $K_2Cr_2O_7$. Ca and Mg do not interfere.

1387. Wavelet (*J. C. S.*, lxiv., ii., 597).—Titrate with $Pb(NO_3)_2$, using KI as indicator.

1388. Lindemann and Motten (*J. C. S.*, lxx., ii., 388).—P_2O_5 is precipitated as ammonio-manganese phosphate; the Mn converted to MnO_2 and estimated iodometrically.

1389. Christenson (*J. C. S.*, lxxii., ii., 282).—From a mixture of $KBrO_3$ and KI, phosphoric acid liberates I, which is estimated with thiosulphate.

1390. Davy (*C. N.*, i., 181).—To acetic solution of the P add ferric oxychloride, using gallic acid as spot indicator. $FePO_4$ is precipitated.

1391. Spica (*J. C. S.*, lxii., 912; and lxiv., ii., 299).—Titrate neutral solution with iron alum, the amethyst colour with salicylic acid being used as indicator.

1392. Burnard (*C. N.*, xvii., 99).—Titrate with uranium nitrate. The delicacy of the ferrocyanide indicator is increased by drying and then again moistening with water.

1393. Joulie (*C. N.*, xxvii., 228, &c.).—Titration with Ur with or without citro-magnesic precipitation, according as Fe, Al, &c., are present or not. Process 1196 is interfered with by H_2SO_4. Examines best conditions for Mg precipitation from citrate solutions. (*C. N.*, lii., 85).—Improved citro-Mg precipitation. Reasons for avoiding estimation as $Mg_2P_2O_7$. HF and HCl interfere with Mo precipitation.

1394. Ville (*C. N.*, xxx., 200).—As 1393. Particularising the estimation in the presence of Ca, Al, and Fe.

1395. Guerin (*C. N.*, xlv., 175).—The Ur solution should be standardised under such conditions as obtain in practice. AmA to be avoided. Also Mohr (*C. N.*, xlv., 248).—Fe separated with ferrocyanide.

1396. Brockmann and Haswell (*C. N.*, xlvii., 177).—The value per c.c. of the Ur solution varies with the amount used.

1397. Mallot (*C. N.*, lxv., 52).—Separate from Fe with Mo; titrate Mg precipitate with Ur in the presence of cochineal, which marks the end by forming a bluish green colour.

1398. Spencer (*J. C. S.*, xlviii., 436)—Add Ag_2CO_3 to faintly acid solution, dissolve Ag_3PO_4 in HNO_3, add $NaCl_2$, and titrate P_2O_5 with Ur.

1399. Firby (*C. N.*, lxvi., 293).—The Ur volumetric process 1393 is unreliable.

IV. Miscellaneous.

1400. Gruner (*C. N.*, xxi., 142).—Very small amounts of P are detected by acting on the metal with acid and observing the spectrum of the burning hydrogen.

1401. Allen (*C. N.*, xxiv., 119).—P and As, when precipitated with Mg, are distinguished by adding $AgNO_3$ to the washed crystals. Acetic acid intensifies the reaction.

1402. Blair (*C. N.*, lvi., 227).—Sketches the various methods proposed for estimating P, and states some precautions for making the "acetate" and "molybdate" estimations.

1403. Waller (*C. N.*, lx., 117 and 131).—Particulars of processes used by fifteen analysts on samples of pig-iron. "The Lundberg (Law) Case."

1404. Arth (*C. N.*, lxii., 155) and Martinotti (*J. C. S.*, lx., 1397).—The results of highly phosphoric slags may be vitiated by the formation of a hydrated ferric phosphate when the HCl is being eliminated by HNO_3.

1405. The following references relate to the state in which P exists in irons:—Schneider (*J. I. S. I.*, 1886, 913; and *J. S. C. I.*, 1888, 125), Cheever (*J. I. S. I.*, 1897, i., 401 and 467; and ii., 290), Juptner (*J. I. S. I.*, 1894. ii., 487; and 1897, i., 224), Campbell and Babcock (*J. I. S. I.*, 1897, ii., 492), and Stead (*C. N.*, lxxxii., 221, &c.; and *J. I. S. I.*, 1900, ii.).

(End of part ix.).

NOTICES OF BOOKS.

The Century Dictionary. An Encyclopedic Lexicon of the English Language. Prepared under the superintendence of William Dwight Whitney, Ph.D., LLD. In Eight Volumes. London: *The Times.* New York: The Century Company. 1899.

The magnitude of this work raises it far above the ranks of ordinary dictionaries, and it truly deserves the title of "An Encyclopædic Lexicon of the English Language." It comprises eight large quarto volumes with 7200 pages of three columns each, 225,000 headings, 100,000 encyclopædic articles, 300,000 quotations, 7500 illustrations, and 500,000 definitions.

The aim of the "Century Dictionary"—we quote from its preface—"includes three things; the construction of a general dictionary of the English language; a more complete collection of the technical terms of the various sciences, arts, trades, and professions than has yet been attempted; and the addition to the definitions proper of such related encyclopædic matter, with pictorial illustrations, as shall constitute a convenient book of general reference." In other words, "The Century" is not only a dictionary, but is a handbook of comprehensive information on all the thousand and one subjects of every-day interest.

We have carefully looked through the volumes of this dictionary with especial regard to chemical and general scientific terms, and we are bound to say that, while nothing material is omitted, the definitions in all cases are characterised by accuracy and completeness.

Indeed we have nothing but praise for the articles we have turned to as tests in these directions, and we know of no other work of a similar character in which so much real information can be found in so short a time. In many cases we have sought for scientific information in "The Century Dictionary" for which we had looked in vain in other works.

There is, however, one point which has already been mentioned in the daily press, a point which we cannot pass over without a few remarks; we allude to the unsatisfactory and inconsistent plan of spelling adopted. In a publisher's note on the first page we read that:—"Having been originally published in the United States the American spelling is preserved." This may have been the intention of the publishers, but we cannot agree that they have carried it out.

Thus, in vol. i., p. 692, we find "Bromine," "a non metallic element allied in its chemical relations to chlorine and iodine." Also, in vol. iv., p. 3178, we find "Iodine," and in the description which follows we are told that "iodine has a very acrid taste, and its odor somewhat resembles that of chlorin." In neither case is there any explanation given that the alternative mode of spelling, "bromin" and "iodin," is used in America. The compounds also of bromine and iodine are called bromides and iodides, with no hint of omitting the final *e*. Turning now to chlorine we see, at vol. ii., p. 971, "Chlorine, See Chlorin," and on looking back we see "Chlorin, Chlorine," while in the description the final *e* is dropped universally in the name of the element itself, and also in the names of the "chlorids." Fluorine occupies an in-

termediate position. The element itself, vol. iii., p. 2288, is "Fluorine, Fluorin," and in the description the final *e* is dropped, although in the preceding heading we find, "Fluoride, a compound of fluorin with another element."

In the description of fluorine we find almost the only want of accuracy we have come across. It is said to be "a gaseous element, not known in a free state, since its isolation is a matter of great difficulty and of some doubt." Considering that Moissan's classical work on Fluorine has been before the world for about fifteen years this is a slip which certainly ought not to occur in so generally accurate a work.

Another error is to be found in connection with the word "sulphur." We have the authority of Prof. Carrington Bolton for stating that the correct *American* method of spelling this word is "sulfur," and yet in this American dictionary which claims to have preserved the American spelling we find the words "sulfer," "sulfur," and "sulpher" all given as obsolete, and the English word "sulphur" is retained as being correct.

May we point out one more slip? On the title-page this work is described as an "*Encyclopedic* Lexicon," yet in "Words and Things"—the advertising specimen pamphlet issued by the *Times*—we find the word "*Encyclopædic*" used throughout.

These lapses, however, do not detract to any appreciable extent from the high standard of excellence which characterises the whole work. As we have already stated, the general scientific information is eminently trustworthy, accurate, and concise.

Tables of Colour and Solubility of Simple Salts. By Henry W. Hill. Reprinted from "Chemistry for Examinations."

These tables have been prepared to exhibit at a glance the colour, solubility, and a few other particulars of the simple salts; double salts and basic compounds have not been included in the list in order to avoid extreme complexity.

The author specially points out that many substances assume different colours when they form crystals containing water of crystallisation, and it has therefore been considered advisable to ascribe two colours to such substances if both forms are likely to be met with. The tables are conveniently arranged, and printed on stout card, folded so as to be easily carried in the pocket.

CORRESPONDENCE.

TAUTOMERISM.

To the Editor of the Chemical News.

Sir,—From a perusal of the abstracts of the papers read at the meeting of the Chemical Society on April 18th (Chem. News, lxxxiii., 223), I note that the rule which I mentioned in my letter appearing in the Chemical News of May 3rd (p. 213) had already been discovered by Dr. Lapworth in 1898 (*Trans.*, lxxiii., 448). I therefore apologise to Dr. Lapworth for overlooking his papers on this subject.

Dr. Lapworth attempts to bring all cases of tautomerism under the general formula—

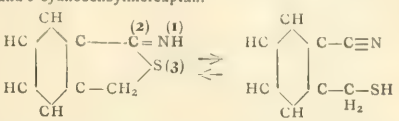
$$M\,R_\alpha \cdot R_\beta : R_\gamma \rightleftarrows R_\alpha : R_\beta \cdot R_\gamma\,M.$$

This general formula is a needless limit.

(A). Of course tautomerism is impossible in an open chain compound wherein the carbon atoms are only united to one another by single linkages, for then, as a result of migration, total decomposition would ensue, *e.g.*,

$$H\cdot O\cdot \overset{H_2}{\overset{|}{C}}\cdot C \rightarrow OCH_2 + CH_4.$$

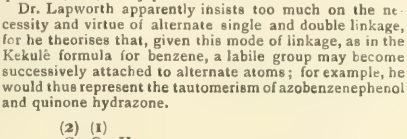
(B). Nevertheless such a general formula does not include a type of change apparently overlooked by Dr. Lapworth; for example, the tautomerism of imidothiophthalide and *o*-cyanobenzylmercaptan.



It is to be noted that it is impossible for the hydrogen atom to travel back via the benzene ring (see A). In fact, no general formula of tautomerism is possible; the labile atom or radicle is necessitated to move 1:3 simply and solely because this is the only movement allowed by valency, and there is no virtue in alternate single and double linking.

It is on this type (B) that I based my conclusions re quinones, &c., in my previous letter.

Dr. Lapworth apparently insists too much on the necessity and virtue of alternate single and double linkage, for he theorises that, given this mode of linkage, as in the Kekulé formula for benzene, a labile group may become successively attached to alternate atoms; for example, he would thus represent the tautomerism of azobenzenephenol and quinone hydrazone.



Firstly, we do not know of any case of tautomerism which really necessitates the above extension, and therefore it is only theoretical; and secondly, if the hydrogen atom does really travel in this way, we ought to have the existence of intermediate tautomerides, but the existence of these has never been demonstrated.—I am, &c.,

A. Lionel Landau.

20, Highbury New Park, N.
June 20, 1901.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxii., No. 22, June 5, 1901.

The Neutralisation of Phosphoric Acid.—M. Berthelot.—The author's present research is chiefly concerned with a study of the double decompositions taking place between chlorides of calcium, barium, magnesium, or silver nitrate and varying proportions of free phosphoric acid, monosodic, bisodic, and trisodic phosphates, or monammonic, biammonic, and triammonic phosphates, the amount of acid being determined in each case by titration at the end of the experiment.

Alloys of Gold and Silver and various other Materials found in Egyptian Tombs.—M. Berthelot.—The author examines (1) a small fragment of gold from the tomb of King Horus of Dahchour, XIII. Dynasty, and finds it to give on analysis—Gold, 92·7 per cent; silver, 4·9 per cent; other substances, 2·4 per cent. (2). Two little metallic leaves, red, yellow, and silver, which give varying proportions of gold and silver.

Tellurides of Gold and Silver found in the Region of Kalgoorlie (East of Western Australia).—Ad. Carnot.—The author examines a number of specimens of silver and gold tellurides from the region of Kalgoorlie. He finds by analysis that these may be divided into the following varieties:—Sylvanite, which is a bitelluride of gold and silver, $(AuAg)Te_2$, having a crystalline texture. Calaverite, a bitelluride analogous to the preceding, but much less crystalline and containing a less proportion of silver. Coolgardite, or sesquitelluride of gold, silver, and mercury, $(Au,Ag,Hg)_2Fe_3$, with varying proportions of gold and silver, which can be substituted for one another to a great extent. Kalgoorlite, $(Au,Ag,Hg)_2Fe$, where the relative proportions of the metals are similarly variable.

Alloys of Aluminium. Compounds of Aluminium and Molybdenum.—Léon Guillet.—The author gives an account of the results obtained during the reduction of molybdic acid by a greater or less excess of aluminium under the same conditions as those described in a former paper (*Comptes Rendus*, May 6, 1901). The experiment is limited on the one side by the reaction corresponding to the production of the metal and on the other side by the reaction giving theoretically Al_6Mo. The experiments are as dangerous as those performed with tungstic acid.

Alloys of Aluminium and Magnesium.—M. Boudouard.—The author examines the alloys of aluminium and magnesium, by the new method of scientific investigation by which the chemical constitution of the alloys is determined. Amongst the physical properties which appear to lead to precise results on the chemical constitution of alloys, the principal are the crystalline structure, the conductibility, electromotive force of dissolution, and fusibility. The author specially takes up the study of the fusibility of alloys of magnesium and aluminium.

Cellular Structure of certain Metals.—G. Cartaud.—The author's experiments were carried out on the easily fusible metals, lead, tin, zinc, cadmium, and bismuth. The metal was melted and then poured on inclined glass plates, so that it cools in thin layers. Under these conditions the free surface of the metal is not homogeneous. Examined with a magnifying power of about 200 diameters bismuth is seen to be crystalline, but in all the other metals examined the surface is covered with a continuous network of cells, having polygonous outlines. Examination of these and other bodies seems to point to the fact that the cellular structure is the normal structure of all amorphous bodies.

Acidimetry of Phosphoric Acid by Baryta, Strontium Oxide, and Lime.—T. Cavalier.—When phosphoric acid is titrated with the bases of the alkaline earths the end points are very variable, not only varying with dilution, but also with the manner in which saturation is effected, and chiefly with the nature of the base. The author endeavours to find the precise conditions under which the alkaline earths can be used for the titration of free phosphoric acid, and if it is possible to observe an end point corresponding to total saturation of the three acidities. The results obtained when solutions of baryta, strontium oxide, and lime, whose concentration varies from $\frac{1}{10}$th to $\frac{1}{100}$th normal, are poured into a solution of $\frac{1}{3}$th normal phosphoric acid, are given in detail.

Alumina Contained in Mineral Waters.—F. Parmentier.—The presence of alumina in any water can be detected in the solid residue. The solid particles should be placed at the bottom of a large glass vessel of distilled water, and small quantities of hydrochloric acid added. The particles of alumina rise to the surface of the water, carried by the bubbles of carbon dioxide.

Action of Isobutylene Bromide on Benzene in presence of Aluminium Chloride.—F. Bodroux.—The result of the author's experiment agrees with theory. The hydrocarbide, $C_{16}H_{18}$, obtained is phenyl-1-dimethyl-2-ethane phenyl, and it is this substance which is partially destroyed under the influence of $AlCl_3$, giving rise to isobutyl benzene. This decomposing action of $AlCl_3$ is exercised in a similar manner on diphenyl-1.2-propane; the chief result being the detachment of the benzenic radicle united to a quaternary carbon.

Action of Alcoylmalonic Ethers on Diazoic Chlorides.—G. Favrel.—The alcoylmalonic ethers react on the diazoic chlorides in the same manner as the substituted cyanacetic ethers, but, whilst the latter furnish pyruvic nitrile hydrazones, the former give the acids corresponding to their ethers.

A New Method of Decomposing Bisulphitic Derivatives.—P. Freundler and L. Bunel.—The authors establish the fact that the alkaline nitrites possess the same property, and are capable of being, under certain conditions, substituted for the carbonates. Experiments show that the decomposition of bisulphitic derivatives by means of nitrites furnishes yields at least equal to those obtained when the carbonate is used.

Secondary Products formed during the Action of Sulphuric Acid on Wood Charcoal.—A. Verneuil.—The two principal acids formed when sulphuric acid acts on wood charcoal are mellic acid and benzenepentacarbonic acid. The author examines the latter product after obtaining it in a pure state.

MISCELLANEOUS.

Society of Arts.—The Annual General Meeting of the Society of Arts was held on Wednesday, the 26th inst., at the Society's House in the Adelphi. Fifty-seven members were elected, this making the total elected during the present session of the Society 376. The Report of the Council was read by the Secretary. It summarised the proceedings of the Society during the last twelve months, giving an account of the various papers which had been read, and the work of the Society's different Committees. Amongst other matters referred to was the resignation of the Presidentship of the Society by the King, who, as Prince of Wales, held the office from 1863. His Majesty, however, while ceasing to be President, has become Patron of the Society. On the occasion of his resignation the Council presented to His Majesty the Society's Albert Medal, which during the past forty years has been awarded to a number of men distinguished for their scientific eminence, or for their services to industry and the arts. During the year a Committee of the Society has produced an important report on Leather for Bookbinding, which will be published in few days. This Committee has determined the causes which produce decay in modern leather bookbindings, and recommends a method of manufacture which ought to be free from the usual defects. Over 15,000 candidates entered for the Society's annual examinations, the results of which are now in course of issue. At the conclusion of the reading of the Report the result of the ballot for the election of the new Council was announced, the President for the coming year being Sir Frederick Bramwell, Bart., F.R.S.

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THE

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VOLUME LXXXIV.

EDITED BY SIR WILLIAM CROOKES, F.R.S., &c.

No. 2171.—JULY 5, 1901.

EUROPIUM: A NEW ELEMENT.

By EUG. DEMARCAY.

In 1885 Sir William Crookes (*Phil. Trans.*, vol. clxxvi., p. 691), during his beautiful researches on electric phosphorescence *in vacuo*, noticed a band which he attributed to samarium, and which by reason of its disappearance in presence of lime, and from certain other peculiarities, he called the "anomalous line." Later (*Journ. Chem. Soc.*, 1889, President's Address), he distinguished this, together with a large number of other bands, as belonging each to a special meta element. The hypothetical meta element corresponding to the anomalous line he called S_3. M. Lecoq de Boisbaudran, in the course of his important researches on phosphorescence, confirmed the above statements with regard to this anomalous line.

In 1892 M. de Boisbaudran (*Comptes Rendus*, 1892, p. 575), described a spectrum consisting of three brilliant blue lines, discovered in the spark spectrum of samarium. These three lines can be reinforced by suitable fractionation. He therefore concluded that they correspond to a particular element Z_ε. About the same time he also drew attention (*Comptes Rendus*, 1893, I., pp. 671—674; II., 199), to a particular band in the reversal spectrum of samarium, which apparently corresponds to the anomalous line, and is considerably reinforced in nitric solution. M. de Boisbaudran, without forming very precise conclusions, inclined to the idea that this line was due to a particular element Z_ζ.

In 1896 (*Comptes Rendus*, vol. cxxii., p. 728), I discovered the presence of an element intermediate between gadolinium and samarium characterised by several strong lines in the violet and ultra-violet. In 1900 (*Comptes Rendus*, cxxx., p. 1469), I showed that this new element was identical with de Boisbaudran's Z_ε, and that Crookes's anomalous band was due to the same substance (see Note), as well as the reversal line Z_ζ, and various other reversal lines not yet identified. I found also that this new element had a special absorption spectrum previously unnoticed. I may add that it has not been possible to carry the fractionations far enough to affirm absolutely that all these properties correspond to the same substance. Since that period, by a long series of fractionations with magnesium nitrate, I have been able to accumulate a considerable quantity of this element, and so able to confirm its various characteristics, and the following spectra:—Reversal, absorption, electric phosphorescence of the sulphate in vacuum (anomalous line), of the sulphate, together with calcium sulphate or gadolinium, which accompanies it in nearly all cases. The properties remain sensibly constant, and evidently characterise the same element. The purity of several grammes of the new oxide was sufficient to show no samarium lines and mere traces of the gadolinium lines.

When traces of calcium sulphate are added to this pure product a brilliant phosphorescent spectrum is produced, in which the anomalous line appears. (See Note).

This spectrum contains three principal bands:—

$\lambda = 609$ about.	Very strong.
$\lambda = 576$,,	Wide and well marked.
$\lambda = 593$,,	Strong, very wide.

The degree of calcination of the mixed sulphate causes a variation in the appearance and the size of the bands. The strongest apparently is converted into a double line when the sulphates are raised to a very high temperature. The spectrum of samarium (especially the red line) was quite invisible. In the gadolinium sulphate the most brilliant lines formed an analogous system, but more complicated. With strongly calcined alumina the spectrum is formed of very brilliant thin lines. I have not yet been able to measure the lines of these spectra. These apparently contradictory results of Crookes and de Boisbaudran are due, I think, to the very small proportions of $\Sigma - Z_\varepsilon$ contained in their material, and that the calcium and gadolinium present reinforced the samarium spectrum rather than the other.

I propose the name europium for the new element, with symbol Eu and atomic weight 151 (approx.).

Below is a list of the strongest lines in the spectrum of europium comprised between $\lambda = 500$ and $\lambda = 350$. The strongest are in the list of the samarium lines given by Exner and Haschek. I repeat that in my spectrum the true samarium lines were absolutely wanting, and the strongest gadolinium lines only just visible:—

λ.	Strength.	λ.	Strength.	
4662·6	12	3819·5	15	
4627·8	13	3815·2	5	
4594·5	14	3817·4	5	
4435·8	16	3781·1	5	
4355·5	7	3741·0	5	
4205·4	16	3724·5	13	
4173·2	5	3688·3	11	
4130·0	15·5	3629·9	7	
4062·3	5	3622·5	5	
4057·8	6	3616·1	5	
4017·6	6	3570·0	6	
4012·7	5	3549·7	7	Near a strong more refrangible ray of Gd.
4011·8	7			
3988·4	6 (wide)			
3972·0	15			
3943·2	7	3547·6	5	
3930·7	15	3543·9	9	
3907·2	14	3541·2	5	
3877·4	5	3530·8	6	
3861·3	6	3520·6	12	
3854·7	5	3530·8	5	

Besides the above mentioned lines which I believe to belong definitely to europium are a very large number of weaker lines, the greater portion being extremely feeble. Much greater doubt naturally exists as to the origin of these lines, which nevertheless disappear from the spectrum if the europium is not very pure. I believe them to belong to this element, though it is possible to suppose that they belong to an unknown element present in minute quantities, even relatively to europium, which is itself so rare. Further investigation is necessary on this matter.

For the lines of the reversal spectrum and the absorption spectrum of europium salts I must refer to my previous paper already quoted.—*Comptes Rendus*, No. 24, June 17th, 1901, vol. cxxxii.

[Note.—It is necessary for me to make one or two corrections to the paper of M. Demarçay.

1. I have never admitted that the body called by M. de Boisbaudran Z_ϵ is the same body which gives my "anomalous line." Indeed, I have good reason to think they are quite different. The line given by M. de Boisbaudran's Z_ϵ is broad and indistinct at the edges, while the "anomalous line" is absolutely sharp and narrow, like a gas line. Also, their refrangibilities are not identical. The same remarks will apply to the body described by M. Demarçay in his 1900 paper.

2. Fifteen years ago I stated (*Proc. Roy. Soc.*, vol xl., p. 505) that a little calcium sulphate entirely suppressed the "anomalous line."—W. Crookes].

A FEW CONSIDERATIONS ON THE ATOMIC WEIGHTS.

By Dr. T. L. PHIPSON.

During the last half century we have seen a great number of laborious experiments, made with the view of determining what are termed "the true atomic weights" of the elements. In future this kind of labour will be saved to a great extent by the perusal of the remarkable work of Gustavus Hinrichs, M.D., LL.D., Professor of Chemistry in the St. Louis College of Pharmacy.

Dr. Hinrichs has devoted a great portion of his studious life to this subject, and we have now in his work, published in 1894, and entitled "The True Atomic Weights of the Chemical Elements," the results of his long and valuable experience.

To an English chemist who, by a stroke of genius, gave us what is universally known as "the law of Prout," our science owes a great deal, and it has been part of Prof. Hinrichs's task to show not only to what an extent chemical science is indebted to Dr. Prout, but how vain have been all the efforts made with the view of proving his law incorrect.

Whilst admiring the perseverance of such ambitious men as the late M. Stas, of Brussels, and his various disciples in England and Germany, Hinrichs points out very clearly that all these laborious determinations of atomic weights of well known elements, when analysed by the aid of one of the simplest of mathematical formulæ, show in favour of Dr. Prout's hypothesis, instead of against it, and tend towards the theory of the "Unity of Matter."

By the severe criticism given in this work of certain results published by Ostwald, Richards, and others, and by pointing out better results previously obtained by Berzelius, Struve, Marchand, Dumas, and Marignac, he will, doubtless, have opened the eyes of the younger generation of scientific chemists who may some day feel inclined to undertake researches of this description. Moreover, the absurdity of replacing the old round numbers of the text-books by these numbers and a fraction, as has been done recently by some German periodicals, is now thoroughly brought to light.

It is painful to all those who have at heart the welfare of chemical science to find a certain number of blind enthusiasts attempting to substitute the uncertain figures obtained experimentally by Stas for those which the true scientist knows must be nearest the truth. For a long series of years the practical analyst in Great Britain has been satisfied with the small and mostly whole numbers derived from the law of Prout. Whilst Continental chemists adopted O=100, we in England made H=1 (and for all practical purposes that is quite sufficient). Now, and for many years past, foreign nations have followed our example in this respect.

It should not be forgotton that, in this world, absolute perfection is denied to us, though we naturally strive to approach it as nearly as possible. The laborious efforts of Stas and his followers have, unfortunately, done harm to science, as Prof. Hinrichs clearly demonstrates in the admirable work which I have named.

It is impossible here to quote detached passages; it must be read as a whole; but it may be stated that the upshot of this truly wonderful book is to prove that the figures published by Stas, when considered from a mathematical point of view, are of no value to the science of chemistry.

With regard to the fact that the law of Prout points to a confirmation of the theory of the "Unity of Matter," this is to be gleaned already from the excellent "Elements of Chemistry," published in 1855, by the late Dr. Gregory, Professor of Chemistry in the University of Edinburgh. When I published in 1886 my "Outlines of a New Atomic Theory," recently reprinted as an appendix to my little work "Researches on the Earth's Atmosphere," I was not aware that some twenty years or more previously similar views had been held by Prof. Gustavus Hinrichs. He imagined the existence of a body which would have half the atomic weight of H, and called it "pantogen," declaring at the same time that with such a substance (which may some day be discovered), the law of Prout will remain as perfect as Newton's theory of gravitation.

In my little sketch I have merely endeavoured to demonstrate that the atoms of all substances are of the *same size* and *same weight*, and that difference of properties of various substances is owing to their "phlogiston," that is, *the distance* (space, energy), at which the atoms are placed. H being the substance in which the atoms are at the greatest distance—which has the greatest amount of "phlogiston"—is also the most energetic body hitherto discovered. C, H, N, and O are, of all the elements, those which contain the most "phlogiston," possess the greatest energy and nearest approach to vitality; hence they form the whole of organic nature.

In the last annual address to the Paris Academy, by the President, these views are alluded to as likely to lead to new and interesting developments.

POTASSIUM PERSELENATE.*

(Preliminary Note).

By L. M. DENNIS and O. W. BROWN.

Potassium perselenate was prepared by the electrolysis of a saturated solution of potassium selenate containing a little free selenic acid. This solution was placed in a 150 c.c. beaker, and the anode, a platinum plate of about 15 sq. c.m. surface, was introduced into it. The cathode, a piece of platinum foil, was contained in a small porous cup of about 75 c.c. capacity which was suspended in the solution. This porous cup was filled with a dilute solu-

* The experimental work herein described was performed by Mr. Brown in the spring of 1898. It has been impossible to resume the work until recently, but it is hoped that the investigation may soon be carried to completion.

tion of selenic acid. The beaker was placed in a freezing-mixture, and a current varying from 2·5 to 3 ampères was passed through the solution. The temperature in the outer cell averaged about 4° C.

After the action of the current had continued for some hours, a white substance began to appear in the neighbourhood of the anode, its formation being accompanied by an increase in the resistance of the cell. After considerable of the solid had separated, the process was interrupted, the solution in the beaker was decanted, and the substance dried on a porous plate. It was then placed in a desiccator containing phosphorus pentoxide, and this was placed upon ice.

The complete analysis of the substance was not made at the time, but merely the available oxygen was determined, this being done, first by adding oxalic acid in excess, and determining the excess by means of potassium permanganate, and second, by adding ammonium ferrous sulphate in excess, and titrating this excess in the same manner.

The two methods gave agreeing results, for when used on a sample of potassium selenate containing a small amount of perselenate, oxalic acid, and potassium permanganate, showed 2·41 per cent of $KSeO_4$, while the ammonium ferrous sulphate method gave 2·42 per cent.

Potassium perselenate was not obtained free from selenate, the highest percentage of perselenate in the product being 74·44.

Potassium perselenate, when hot, oxidises manganese dioxide to potassium permanganate, quickly oxidises ferrous sulphate in the cold, and acts similarly upon thallous sulphate. An aqueous solution of the salt gives off oxygen when warmed.—*Journal of the American Chemical Society*, vol. xxiii., No. 5.

ON THE SEPARATION OF TUNGSTIC AND SILICIC ACIDS.*

By H. L. WELLS and F. J. METZGER.

In a recent number of a German periodical (*Ztschr. Angew. Chem.*, 1901, 165), appears an article by Otto Herting, of Philadelphia, in which the assertion is made that the method given in the text-books for expelling silica from tungstic acid by means of hydrofluoric acid is incorrect. This statement is made on the ground of alleged numerous quantitative experiments with mixtures of pure tungstic acid and pure ignited silicic acid, but no details in regard to the results are given. Herting believes that, upon ignition, silicic and tungstic acids form a silicotungstic acid which is volatile when treated with hydrofluoric acid, and finally says that he should be pleased if, by means of his article, he should bring about the more careful study of the "action of hydrofluoric acid upon tungstic acid in the presence of silicic acid."

Since Herting's statement throws doubt upon a method that is generally used, we have undertaken an examination of the matter. For this purpose, we dissolved some of Kahlbaum's tungstic acid in ammonia, precipitated with nitric acid, washed with water by decantation, digested repeatedly with sulphuric acid of sp. gr. 1·378 to separate any molybdic acid that might possibly be present (see Ruegenberger and Smith, *Journ. Amer. Chem. Soc.*, xxii., 772), washed the residue, and ignited it. The tungstic acid thus prepared was used for the experiments that follow.

A weighed quantity of tungstic acid in a platinum crucible was mixed with about an equal quantity of pure silica. The mixture was covered with dilute sulphuric acid, a liberal amount of pure hydrofluoric acid added, the liquid carefully evaporated, and the residue ignited over a Bunsen burner. Then another portion of silica was added, and the operation repeated. The results are shown in the following table:—

	Taken.		Tungsten trioxide found after	
	Tungsten trioxide.	Silica.	First operation.	Second operation.
	Grm.	Grm.	Grm.	Grm.
I.	0·1928	0·2	0·1927	0·1928
II.	0·2097	0·2	0·2097	0·2096
III.	0·2100	0·2	0·2099	0·2100
IV.	0·1999	0·2	0·2000	0·1998

The greatest error found in these experiments is 0·0001 grm., and they show that the process is perfectly exact under these conditions.

Other experiments showed that long ignition of the mixed tungstic and silicic acids over the Bunsen burner before expelling the silicic acid had absolutely no effect upon the results. It was thought that in the absence of sulphuric acid a loss might occur by the treatment of tungstic acid with hydrofluoric acid, and the following experiments were made to test this point, no sulphuric acid being used:—

Taken.		
Tungsten trioxide.	Silica.	Tungsten trioxide found.
Grm.	Grm.	Grm.
0·1983	0·2	0·1983
0·2102	0·2	0·2100
0·2106	0·2	0·2105
0·1996	0·2	0·1994

In these experiments, the greatest error, 0·0002 grm., is well within reasonable limits; hence, it is evident that the absence of sulphuric acid has no effect. It is to be noticed that in these cases also, the tungstic acid was ignited by the Bunsen flame only.

Attention should be called to the fact that tungstic acid must not be ignited by means of the blast-lamp, since at the temperature thus produced, it volatilises to a considerable extent. The books of reference do not give proper warning in regard to this matter. The following table gives the results of a series of experiments made by heating some of the substance (which showed no loss of weight over the Bunsen burner), over the blast-lamp in a platinum crucible:—

	Weight of tungsten trioxide. Grm.	Loss. Grm.
Taken	0·3007	—
Ignited for two minutes	0·2978	0·0029
" " " " again..	0·2962	0·0016
" " " " "	0·2946	0·0016
" " " " "	0·2932	0·0014
" " " " "	0·2924	0·0008
" " " " "	0·2916	0·0008
" " " " "	0·2906	0·0010
" " five " "	0·2872	0·0034
Total loss ..		0·0135

All the ignitions except the last were made with a lamp provided with a water-blast, which gave a flame of only moderate power. The last ignition was made with a lamp connected with a foot bellows, which gave a considerably higher temperature. It is noticeable that the losses show a tendency to diminish after the first ignition, but this is probably due to a change in the physical condition of the oxide rather than to the removal of some more volatile substance. It is hardly possible that our carefully purified tungstic acid, which showed no loss when heated with a good Bunsen burner, could contain an amount of molybdic acid or other volatile substance sufficient to give the results that have been obtained. The loss shown in the table above amounts to nearly 5 per cent., while in another experiment 0·1955 grm. of tungstic acid lost over 7 per cent after heating with the blast-lamp for twenty

* Contribution from the Sheffield Laboratory of Yale University. From the *Journal of the American Chemical Society*, xxiii., No. 5.

minutes. It should be stated that the platinum crucible in which these ignitions were made showed no loss in weight after it had been cleaned.

We have shown that Herting's criticism of the usual method for separating silicic and tungstic acids is without foundation, and it appears probable that his difficulties were due to igniting tungstic acid at a too elevated temperature.

ON THE METEORIC STONES WHICH FELL NEAR ZOMBA, BRITISH CENTRAL AFRICA, ON JANUARY 25TH, 1899. WITH NOTES ON THE CHEMICAL ANALYSIS OF SUCH BODIES.*

By L. FLETCHER, M.A., F.G.S.,
Keeper of Minerals in the British Museum.

PART I.—THE CIRCUMSTANCES OF THE FALL OF THE STONES.

On January 25th, 1899, at 7 54 a.m., a loud noise as of an explosion was heard at the settlement of Zomba, British Central Africa, and for many miles around; almost simultaneously therewith, several small stones were seen to reach the earth in the neighbourhood of Zomba and were collected by the observers of their fall.

Mr. Alfred Sharpe, C.B., His Majesty's Commissioner and Consul-General for the Protectorate of British Central Africa, Mr. J. F. Cunningham, Secretary to the Administration, and Mr. J. McClounie, the Acting Collector of Revenues, on hearing the detonation, surmised that it had an origin in the entry of a meteorite into the earth's atmosphere, and with praiseworthy zeal and energy at once proceeded to collect, by aid of the telegraph and by personal interviews with the witnesses, all the reliable evidence that could be obtained relative to so extraordinary a phenomenon. A Report, embodying this information and the notes made by Mr. Cunningham and Mr. McClounie, was sent by Mr. Sharpe to the British Museum; four of the stones, generously presented by Mr. Sharpe, Mr. Cunningham, and Mr. McClounie, were forwarded at the same time for scientific examination, and for subsequent preservation in the Meteorite Collection of the Museum

The details given in the Report may be classified as follows:—

Luminous Meteor and Trail.

(*Zomba*). "There being much cloud at the time, nothing was visible to indicate that a meteorite had entered the earth's atmosphere."

(*Blantyre*). "A native named Bwanali, who was sitting in the open near the Government buildings, saw, a little before 8 a.m., a star of exceptional brilliancy pass across the sky in the direction of Lake Shirwa (roughly, west to east)." "A native capitao in the employment of Mr. James Lindsay makes a similar statement, and adds—it left a trail or tail behind it."

(*Chiromo*). "Mr. H. C. McDonald telegraphed that several natives saw the star and smoke. They stated that it appeared to pass over Cholo."

(*Fort Johnston*). "Mr. O. C. Ockenden, the Acting British Vice-Consul, telegraphed that the meteorite had been seen from Fort Johnston."

(*Chengali's village*). "Sergeant-Major Bandawe, of the British Central African Rifles, who was on his way to Zomba, saw the meteor when he was at Chengali's village to the West of Lake Pamalombe. It left a trail, and exploded in the direction of Chikala."

Owing to the cloudy state of the sky the luminous meteor was thus seen from only a small number of places, and presumably for only small portions of its path. It must have been far above the clouds, for it was seen from places 130 miles apart. The meteor appears to have been travelling in an approximately easterly direction, and was seen to explode when near a line drawn from Lake Pamalombe to Chikala.

Detonation.

(a). *Places at which it was heard.*

(*Top of Mt. Zomba*). Mr. Sharpe says:—"I heard one very loud report."

(*Zomba*). "Mr. Cunningham says:—"There was heard a crash like thunder."

(*Blantyre*). "The native Bwanali heard an explosion like a crash of thunder. A native capitao in the employment of Mr. James Lindsay makes a similar statement."

(*Chikwawa*). "Mr. J. O. Bowhill, the Judicial Officer at Chikwawa, heard the explosion as he was standing near his house. It seemed to him to come from the direction of Blantyre."

(*Katunga*). "Mr. C. B. Vertue, the Agent of the African Lakes Company, made inquiries, and states that the explosion was heard by Muri (a native servant), 'James' and Mgano (capitaos), Njeresa and Mpeni (natives in charge of cattle).

"A native from Katunga's village came in to Chikwawa and told the Collector of Revenues that the explosion had been heard in that village."

(*Chiromo*). "Mr. H. C. McDonald telegraphed that several natives heard the explosion."

(*Fort Johnston*). "Mr. O. C. Ockenden telegraphed that the explosion had been heard at Fort Johnston."

As far as could be ascertained, neither the luminous meteor nor the detonation had been remarked by any one at Kota-Kota, Nkata, or Karonga, places which are north of Fort Johnston, and lie on the western shore of Lake Nyasa; they are in telegraphic connection with Zomba.

(b). *Character of the Detonation.*

The character of the detonation as heard by an observer would vary to some extent according to his situation.

(*Zomba*). Mr. J. F. Cunningham says:—"I heard a crash like thunder, the reverberations lasting for a few minutes afterwards. When I heard it, I suspected what it was, but thought it might possibly be a dynamite explosion on the road to the new Residency, where I knew the Road-Engineer, Mr. William Fletcher, and a party of men were at work. I sent an inquiry to Mr. Fletcher, and he sent back word that he also had heard the explosion, but that it had not occurred on the Road."

Mr. J. McClounie says:—"The loud report had the precision of a cannon. I was indoors at the time, but instantly rushed out to see what had happened. My attention was drawn towards the east by the continuous rolling noise. The natives also were looking in an easterly direction."

(*Top of Mount Zomba*). This mountain rises to a height of 6000 feet above the sea, and is on the western side of the settlement, which is itself 2900 feet above the sea. Mr. Sharpe says:—"I heard one very loud report; then for some two minutes a long rumbling or buzzing noise, gradually getting fainter and fainter; I should not call it reverberations."

(*Kuntamba's village*). "The chief Kuntamba, at his village about three miles from the Residency, to the west of the road to Domasi, heard a noise like thunder."

(*Blantyre*). "The native Bwanali heard an explosion like a crash of thunder."

The detonation was thus a single one; at Blantyre and about 50 miles away in the villages north-east of Zomba it was as loud as thunder; it was heard also at Chiromo, about 90 miles south of the settlement of Zomba, and also beyond Fort Johnston, which is at a

* From the *Mineralogical Magazine*, vol. xiii., No. 59, 1901.

distance of 70 miles to the north of Zomba; to the observers at Zomba itself the sound seemed to come from the east.

Fall of Stones.

About an hour after the detonation had been heard, news reached the Residency that several stones had fallen in native villages on the eastern slopes of Mount Zomba. As many as ten were ascertained to have been found, and these have been preserved; only those stones were discovered which fell near to people or houses, and possibly they form only a small proportion of those which actually reached the earth.

The following is the history of the individual stones:—

Stone No. 1. Weight 2 ozs. 57 grms.). Fell at Kuntamba's village, about three miles from the Residency, to the west of the road going to Domasi. The chief Kuntamba gave the following account to Mr. Cunningham:—"This morning I was standing near my house when I heard something fall on the rock there" (pointing to a fairly level slab of granite, measuring 20 feet by 12 feet, near his house). "Immediately after, I heard a noise like thunder. I went to the rock and saw where a stone had fallen, and I picked up some small bits."

Mr. Cunningham adds:—"There was a large crowd of the village people present when the chief told me this, and two of them, Matendu and Laici, personally vouched for its accuracy. The fragment has only a small portion of outer crust. It is the largest of the pieces found at this spot."

Stone No. 2. Weight 4½ ozs. (128 grms.). Fell at Kumpamba's village, 3 miles from the Residency along the Domasi road. The fall was witnessed by the chief and others. It is the smallest of the completely encrusted stones.

Stone No. 3. Weight 1 lb. 3 ozs. (539 grms.) It was seen by a native to fall on the outskirts of the last-mentioned village. It is incomplete, a large piece having been broken off through impact against a stone when it fell. Presented to the British Museum by Mr. McClounie.

Stone No. 4. Weight 3 lbs. 5 ozs. (1502 grms.). Fell on the border of a new garden on the verge of the forest about 400 yards to the south of the Likangala River, near Chiropa's village. A native was hoeing in the garden when the stone fell. The place was stony, and a corner of the meteoric stone was chipped off by the fall.

Stone No. 5. Weight 12½ ozs. (354 grms.). Fell at Kampunga's village on Buchanan's Estate. "It was about noon when we (Mr. Ravenor and Mr. Cox) got to Kampunga's village (to inquire about the stone reported by Mr. Cunningham to have fallen there). We found the village people squatting round the stone in a circle, discussing the 'miracle' as they called it. No one had touched or approached the stone, and when we arrived it was still lying where it had fallen. The story of its advent was given as follows:—'A woman was pounding corn under a tree, within about ten yards of her hut, when the stone fell. The whole village heard the detonation immediately afterwards, and gathered to where the woman was standing to view the stone. They were afraid of it, thinking it enchanted, and they sat at a distance round it, each giving a version of its probable origin and meaning.' It fell on hard ground, but, as there were no rocks about, I (Mr. Ravenor) was able to dig it up complete. It is covered with crust."

Stone No. 6. Weight 5 lbs. 12¼ ozs. (2622 grms.). Fell to the south of the Likangala River, to the west of Stone No. 4. It is the largest stone found, is completely encrusted, and has the usual pittings.

Stone No 7. Weight 1 lb. 13 ozs. (822 grms.). Fell at Chope's village, near Songani. It is probably only part of the fallen stone, for one large surface is not encrusted. Presented by Mr. Cunningham to the British Museum.

Stone No. 8. Weight 1 lb. 6½ ozs. (638 grms.). Fell at Chirunga's village, two miles from the Residency, near the Domasi road. The side shown by a photograph of the stone is completely covered with crust.

Stones Nos. 9 and 10. Weights 14½ ozs. (411 grms.) and 1 lb. 1 oz. (482 grms.), respectively. Both of them fell at Kanyama's village, and have been presented by Mr. Sharpe to the British Museum; they are almost completely encrusted stones. "Several people heard them crashing through the trees, and after a search found first one stone, and, later on, the other."

Mr. McClounie says that one small stone in its fall cut a twig from the branch of a tree; this was two miles from Zomba, off the Liwonde road; several of the other pieces were picked up at or near this place.

As the meteorite travelled in a more or less easterly direction and reached the ground only a short distance from Zomba, and the detonation seemed to the observers of Zomba itself to come from the East, it follows that the detonation is really a consequence of the break-up of the meteorite, and not, as has been sometimes suggested, due to the rush of air into the vacuum left behind the meteorite during its flight.

Area of Distribution of the Stones.

Mr. McClounie says:—"As far as I know at present the area over which the stones have fallen is about 9 miles long and 3 miles wide. Whether any fell outside this area may never be known." (The positions of the stones as indicated in a map, Plate I., must be only approximate).

The dimensions thus assigned by Mr. McClounie are exactly identical with those of the area over which the stones were distributed in the case of the meteoritic fall at Knyahinya, Hungary, on June 9th, 1866. The area of distribution of the stones, in the case of a meteoritic shower, has rarely been found to measure more than ten miles by three.

The two heaviest stones, Nos. 6 and 4, weighing respectively 5 lbs. 12¼ ozs. and 3 lbs. 5 ozs., were found at the southern end of this area. The next largest, No. 7, still weighing 1 lb. 13 ozs., and probably not more than half of the stone which fell, was at the northern end of the area, and not far from the smallest completely encrusted stone, No. 2, weighing 4½ ozs.; the complete stone, No. 7, may have really been the largest which fell. Stones Nos. 9 and 10, weighing respectively 14½ ozs. and 1 lb. 1 oz., were also found north of the smallest stone.

The area of distribution on the earth's surface of the stones of a large meteoritic shower is usually, not always, elongated in the direction of flight of the luminous meteor, and the stones are generally distributed within this area approximately according to size, the larger ones being near the end towards which the meteor's flight was directed. A distribution precisely according to size would be a necessary result of the resistance of the air on the individuals of an at first closely packed swarm of similar meteoric stones moving through the earth's atmosphere in a direction inclined to the vertical, if each stone remain unbroken during its flight. But an admixture of sizes may result in various ways. For instance, a stone may be broken up into scattered unequal fragments at a point in its passage through the atmosphere such that the subsequent path of the fragments is not long enough for the differentiating effect of the resistance of the air to render of no moment their initial scattering in various directions.

Having regard to such considerations, it will be seen that the number of stones found at Zomba is too small, and the sizes are too intermingled to admit of any sound inference as to the direction of the meteor's path from a mere study of the distribution of the fallen material, but the distribution, especially if No 7 was really the largest

stone, is not inconsistent with the direction suggested by the observations already referred to. It seems likely that the stones resulted from the breaking up of a single mass within the earth's atmosphere; there was only one detonation, and presumably only one important epoch of fracture; as the stones are completely encrusted, the scattering of the fragments must have taken place at a point where their velocity was high enough to cause superficial heating to a high temperature. As there is no mention, in the Report, of deep penetration of the ground, it is probable that the velocity was comparatively small at the time of impact on the earth's surface.

Material of the Stones.

It may be added that the material of the stones was observed to be unlike that of any of the rocks of the district, and that the specific gravity of two of the stones was determined by Mr. T. J. Binnie, Acting Chief Surveyor, to be 3·5, which is much higher than that of any of the Zomba rocks; further, Mr. McClounie noticed the numerous metallic particles glittering on the fractured surface, and proved that the material has a directive action on a compass-needle.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 20th, 1901.

Prof. EMERSON REYNOLDS, Sc.D., F.R.S., President, in the Chair.

MESSRS. Jerdan, Blake, Eyre, and Shutt were formally admitted Fellows of the Society.

The following certificates were read for the first time:—Thomas Thorne Baker, 28, Church Road, Forest Hill, S.E.; Edwin Hobson, 3, Oxford Road, Liscard, Cheshire; Charles Harold Johnson, Beaumont, Northcote, Melbourne, Victoria, Australia; Edward Hall Miller, Common Hall, Hadleigh, Essex; Herbert Simpson Newbould, Trinity Hall, Cambridge; Allan Sandford, Market Place, Ulverton.

The PRESIDENT announced that Dr. Armstrong had undertaken to deliver the Frankland Memorial Lecture on Thursday, October 31st, 1901.

ADDRESS TO GLASGOW UNIVERSITY.

The following Address was presented to the University of Glasgow on the occasion of the four hundred and fiftieth anniversary of its foundation:—

"The Chemical Society, as representing Chemical Science in the United Kingdom, desires to congratulate the University of Glasgow on the celebration of the Four Hundred and Fiftieth Anniversary of its foundation.

The Chemical Society recalls with pride the fact that Members of the University of Glasgow have been most distinguished Fellows, and have contributed by their labours, some of which are among the classics of our Science, to the development of chemical learning.

"Thomas Graham, one of the Founders of our Society and our first President, was the most illustrious of the pupils of Thomas Thomson, whose name is honourably connected with Chemistry as head of one of the first Schools of Practical Chemistry established in this Kingdom, a school which he inaugurated within your walls.

"Thomas Anderson, an honoured name with you as a teacher, who was among the earliest to cultivate with an energy and zeal eminently characteristic the newly developed domain of Organic Chemistry, was for many years one of the most active of our Fellows.

"We sincerely trust that your University may continue to flourish in the future as in the past, and that its efforts to foster and promote the Science which we represent may be as successful in the years to come as they have been since the days of Black.

J. EMERSON REYNOLDS, President.
WILLIAM A. TILDEN, Treasurer.
WYNDHAM R. DUNSTAN,
ALEXANDER SCOTT,
RAPHAEL MELDOLA,
} Secretaries."

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Ormsby Gore Adams, Guy Ashwell, Thomas Aspinall, William George Aston, Hubert Haigh Barker, Edwin Sloper Beaven, Fred Bedford, Joseph Samuel Bridges, B.Sc., Arthur Crabtree, George Dean, M.A., Thomas H. J. Eling, B.A., Edward K. Hanson, B.A., Frederick Thomas Harry, Edward Horton, Christopher G. Kiddell, B.A., Robert Tabor Lattey, B.A., Adolf L. F. Lehmann, B.Sc., Ph.D., William Lowson, B.Sc., F. G. Macdonald, Daniel McLaren, B.Sc., Frank Oram, John Powell, B.Sc., John Edward Purvis, M.A., James Bertram Russell, B.Sc., Thomas Sandford, Samuel Edward Sheppard, Gerald T. S. Sichel, Andrew Biggam Smith, John Davidson Spence, Arnold Rowsby Tankard, George William G. Tatam, William Arthur Whitton, James Whittle, and Duncan R. Wilson, B.A.

Of the following papers, those marked * were read:—

*105. "*The Direct Union of Carbon and Hydrogen.*" Part II. By W. A. BONE and D. S. JERDAN.

The authors have already shown (*Trans.*, 1897, lxxi., 41) that carbon and hydrogen combine at 1200°, forming a saturated hydrocarbon; and also that when the electric arc is passed between carbon terminals in an atmosphere of hydrogen, a saturated hydrocarbon is produced in addition to acetylene, the formation of each continuing until a definite equilibrium between acetylene, the saturated hydrocarbon, hydrogen, and carbon vapour is established. It was then provisionally assumed that the saturated hydrocarbon produced both at 1200° and in the arc is methane.

Further experiments have been made in which the saturated hydrocarbons in question have been separated from the large excess of hydrogen (by means of palladium), and also, in the case of the arc gases, from the acetylene simultaneously produced. Analyses of the residual saturated hydrocarbons, mixed with whatever nitrogen was contained in the original hydrogen employed, have shown that whereas the gas obtained by the direct action of hydrogen upon solid carbon at 1200° consists of methane only, the saturated hydrocarbons produced in the arc consist of methane with one of its homologues, which further investigation has shown to be ethane.

The authors are able to show further that in the arc methane and ethane are produced simultaneously, and at rates which bear a constant ratio to one another throughout an experiment, until a definite equilibrium is reached. By calculation from the results of the previous experiments, interpreted in the light of later work, the proportions between the various hydrocarbons and hydrogen when this equilibrium is attained are shown to be:—

Hydrogen	.. .. ..	90—91 per cent
Acetylene	.. .. ..	8—9 ,,
Methane	.. .. ..	1·25 ,,
Ethane	.. .. ..	0·25 ,,

*106. "*Ammonium and Other Imidosulphites.*" By E. DIVERS and M. OGAWA.

The authors have already called attention to the occurrence of ammonium imidosulphite amongst the products of the decomposition of ammonium amidosulphite, and have given some account of the salt (*Proc.*, 1900, xvi., 113). They now separate it by dissolving it out with warm 90 per cent alcohol, after having used 95 per cent alcohol to extract some other crystalline matter and the red substance. By

working in this way, the imidosulphite is obtained at once almost pure, requiring only to be washed with alcohol. It forms minute, very thin, glistening prisms, somewhat deliquescent, neutral to litmus, and of mild sulphurous taste. Heated in the dry state, most of it decomposes, but a little occurs in the sublimate along with pyrosulphite. The residue left on heating it up to 150° consists of sulphur, sulphate, and imidosulphate. The salt is very soluble in water, and slowly decomposes in solution. Boiled with hydrochloric acid, it yields sulphur, sulphur dioxide, and amidosulphuric acid, the sulphur and sulphur dioxide representing, no doubt, decomposed thiosulphate, $2NH(SO_2NH_4)_2 + OH_2 = 2NH_2SO_3NH_4 + S_2O_3(NH_4)_2$. Ammonium imidosulphite gives a barium precipitate soluble in hydrochloric acid. Potassium imidosulphite and barium ammonium imidosulphite have been prepared, and are crystalline soluble salts.

*107. "*Nitrilosulphates.*" By E. Divers and T. Haga.

Ammonium nitrilosulphate cannot be obtained by the sulphonation of ammonia, for the imidosulphate which is the product of the union of sulphur trioxide with ammonia is decomposed by heat only at a very high temperature, and then is radically broken up without giving any nitrilosulphate. The sulphonation of a nitrite first into hydroximidosulphate and then into the nitrile is therefore the only way open. The ammonium and potassium salts were obtained by Fremy (1845), and a potassium sodium salt, $SO_3Na·N(SO_3K)_2$, by Raschig (1887). The ammonium salt, as it has the composition of $4NH_3+3SO_3$, is a very interesting salt, the existence of which had been forgotten. Sodium nitrilosulphate is so very soluble that it has not been isolated before. It can be obtained by passing sulphur dioxide into the most concentrated solution possible, containing sodium nitrite and sodium carbonate in the ratio of two molecules of the former to three of the latter salt, until the new salt begins to crystallise out. It occurs in small, sparkling, short, thick prisms containing $5H_2O$ and is exceedingly unstable. It is neutral to litmus. By dissolving the salt in concentrated, faintly alkaline solution of barium chloride, a precipitate is obtained, flocculent at first, but becoming crystalline and dense, of barium or barium sodium nitrilosulphate.

*108. "*The Decomposition of Hydrocarbons at High Temperatures.*" (Preliminary Note). By W. A. Bone and D. S. Jerdan.

For some months past the authors have been studying the decomposition of various hydrocarbons at a temperature of about 1150°. Since methane is the only hydrocarbon produced by the direct combination of carbon and hydrogen at 1200°, it seemed probable that any hydrocarbon would, at this temperature, be decomposed, yielding ultimately carbon, hydrogen, and a small percentage of methane. So far the authors have only studied the decomposition of methane and acetylene in detail, but the recent publication of a paper "Ueber pyrogenetische Reactionen organischer Substanzen" by W. Ipatiew (*Ber.*, 1901, xxxiv., 496), in which he announces his intention to investigate the decomposition of hydrocarbons at high temperatures, makes it desirable that they should publish this note.

The method adopted by the authors, which will be described in detail in a future communication, consists in admitting the pure hydrocarbon into a vacuous, glazed porcelain tube (length 60 c.m., internal diameter 12 m.m., capacity about 65 c.c.), nearly the whole length of which has been previously heated to about 1150° in a specially designed Fletcher furnace. The experimental tube is properly jacketed so as to prevent any diffusion of furnace gases into it. The temperature, which can be maintained practically constant for several hours, was ascertained by means of a Roberts-Austen electrical pyrometer. After the gas under investigation has been subjected to the high temperature for a definite time, it is quickly pumped out into tubes over mercury.

Acetylene is very rapidly decomposed at 1150°; after one minute not more than 10 per cent, and after five minutes only a mere trace of it remains. Considerable quantities of a saturated hydrocarbon, which subsequent examination has shown to be methane, are formed during the early stages of the decomposition, and afterwards this methane is slowly, though never completely, resolved into its elements. Neither benzene nor ethylene are formed at any stage of the decomposition, and, after the final disappearance of acetylene, the gaseous products contain hydrogen and methane only. Carbon is liberated during the early stages as "lamp-black," which doubtless arises from the rapid decomposition of the acetylene, but afterwards it is only deposited on the inner surface of the tube in a form much resembling "gas carbon."

The following figures show the percentage composition of the gases obtained in a series of experiments in which the time of heating varied from 1 minute to 3 hours:—

Time	1 min.	5 mins.	15 mins.	1¼ hrs.	3 hrs.
Acetylene ..	10·0	trace	nil	nil	nil
Methane ..	16·0	21·5	16·0	7·75	3·0
Hydrogen ..	74·0	88·5	84·0	92·25	97·0

Methane is resolved into its elements at 1150° more rapidly than would be generally supposed. The decomposition, however, only occurs at the surface of the containing tube, where the carbon is deposited in a form much resembling "gas carbon" in appearance. At no stage of the decomposition was it possible to detect the formation of acetylene, ethylene, or any other unsaturated hydrocarbon. A careful examination of the gas left after 15 minutes' heating has shown that it contains no other saturated hydrocarbon than methane. The following figures indicate the percentage composition of the gas obtained at the end of 5, 15, and 30 minutes respectively, leaving out of the reckoning any small amount of nitrogen it contained:—

Time	5	15	30 minutes
Methane	37·5	12 25	6·6
Hydrogen	62·5	87·75	93·4

The authors are now completing a series of experiments on ethane, and then propose to extend the research to other typical hydrocarbons, and to temperatures other than 1150°.

*109. "*Note on the Sugars from Cellulose.*" By Henry J. H. Fenton.

In several previous communications (Fenton and Gostling, *Trans.*, 1898, lxxiii., 554; 1899, lxxv., 423; 1901, lxxix., 361, 807), it has been shown that various forms of "cellulose" (such as filter-paper and cotton) give considerable yields of the chloro- or bromo-derivatives of methylfurfural when they are heated with dry hydrogen chloride or bromide dissolved in an appropriate solvent. It was further shown that the formation of the bromo-derivative in any notable quantity is indicative of the presence of a *ketohexose* nucleus or grouping, and the existence of one or more such groupings in "cellulose" was consequently inferred. Recent experiments indicate that the same observations apply also to the *chloro*-derivative.

After treatment of cellulose in this manner with dry hydrogen chloride and complete removal of the methylfurfural derivative by washing repeatedly with ether, a dark brown residue is left which, in the case of filter-paper, still shows a fibrous structure, and amounts to about 90 per cent of the material taken. If this residue is digested with warm water, a solution is obtained which gives all the reactions of *dextrose*. It is strongly dextrorotatory, and with phenylhydrazine acetate, on heating, yields *glucosazone* (m. p. 204—206°, N = 15·83, theory requiring 15·64 per cent). On evaporating the solution to small bulk in a vacuum, and adding alcohol, a syrup is at once precipitated, which solidifies on standing, and the solution continues to deposit crystalline crusts after a time. Mannose appears to be excluded from the fact that phenylhydrazine gives no precipitate in the cold even after standing for several hours.

Fifty grms. of Swedish filter-paper were treated in the manner above described, the solvent used being carbon tetrachloride, and the resulting chloromethylfurfural estimated by weighing the crystals. The residue was then extracted with water, and the dextrose estimated by means of Fehling's solution. The results gave chloromethylfurfural 3·1 grms., and dextrose 1·57 grms. At first sight therefore it would appear that the methylfurfural derivative is produced in excess. But it is found that when dextrose is treated in the same manner, a considerable portion is destroyed, leaving a black residue. A blank experiment was made with 5 grms. of dextrose under exactly similar conditions, with the result that the carbon tetrachloride extract weighed only 0·01 grm., and the residual sugar 2·2 grms. If it be assumed that the dextrose resulting from the action on cellulose is destroyed to a similar extent, the calculated amount of this sugar produced in the first experiment mentioned would be 3·54 grms. This, it will be seen, is approximately the quantity required (3·86 grms.) on the assumption that the chloromethylfurfural and dextrose are produced in *equal molecular proportions* (144·5 : 180).

These facts appear to be of especial interest in relation to the recent work of Skraup and König (*Ber.*, 1901, xxxiv., 1115), in which it is stated that the cellulose acetate obtained by the action of acetic anhydride and concentrated sulphuric acid on filter-paper is an *octoacetyl biose*, and that this on hydrolysis yields "cellose," $C_{12}H_{22}O_{11}$.

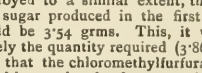
A simple explanation of the results above mentioned would be afforded if it be assumed that this "cellose" (and its antecedent) contains both ketohexose and aldohexose residues, so that the action of hydrogen chloride could be represented by one of the following equations:—

$$C_{12}H_{20}O_{10}+HCl=C_6H_5O_2Cl+C_6H_{12}O_6+2H_2O;$$
$$C_{12}H_{22}O_{11}+HCl=C_6H_5O_2Cl+C_6H_{12}O_6+3H_2O.$$

If the brown residue which remains after extracting the chloromethylfurfural and sugar be dried, and again treated with dry hydrogen chloride as before, a further yield of both products is obtained, and experiments are being made to ascertain to what extent this treatment may be repeated, and what is the nature of the final residue.

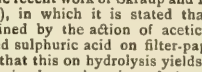
*110. "*Studies in the Camphane Series.*" Part IV. By M. O. Forster.

1-*Benzoxy-2-benzoylcamphene*,—



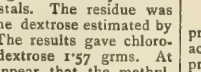
prepared by the action of benzoyl chloride on the sodium derivative of camphor dissolved in toluene, crystallises from alcohol in colourless, highly refractive prisms, and melts at 144°; a 4 per cent solution in chloroform has the specific rotation $[\alpha]_D = +189·7°$.

1-*Hydroxy-2-benzoylcamphene* (*enolic α-benzoylcamphor*),



obtained by hydrolysing the foregoing substance with alcoholic potash, crystallises from alcohol in flattened octahedra, and melts at 89°; a 2 per cent solution in chloroform gave $[\alpha]_D = +281·1°$. It dissolves in sodium carbonate, and an alcoholic solution developes immediately an intense purple colouration with ferric chloride; cold concentrated sulphuric acid and boiling formic acid convert it into the ketonic modification, a change which also proceeds spontaneously when the substance is dissolved in organic media, the transformation into the ketone being accelerated by addition of piperidine or by exposure to sunlight. The *sodium*, *copper*, and *ferric* derivatives are crystalline, and are freely soluble in organic liquids; the *phenylurethane* derivative melts at 117°, and the *acetyl* derivative, which crystallises from alcohol in lustrous, rectangular plates, melts at 107°.

a.Benzoylcamphor,—



produced on boiling a solution of the isomeride in formic acid, crystallises from alcohol in colourless, transparent prisms melting at 87—88°; a 2 per cent solution in chloroform gave $[\alpha]_D = +125·0°$. The alcoholic solution remains indifferent to ferric chloride at first, but a green colour is rapidly developed, and changes ultimately to bluish-violet. Fusion converts the ketone into the enolic isomeride, and the specific rotation of a solution in chloroform gradually increases until $[\alpha]_D = +216°$, the value to which the optical activity of the enol diminishes.

*111. "*On the Decomposition of Carbon Dioxide, when submitted to Electric Discharge at Low Pressures.*" By J. N. Collie, Ph.D.

During some experiments that were being made on the relative resistance of carbon dioxide in a vacuum tube to the electric spark from an induction coil, it was noticed that the resistance varied considerably. At the same time, the colour of the incandescent gases at the negative electrode was seen to change. In order to ascertain what changes had taken place in the composition of the gas after sparking, the contents of the vacuum tube were pumped out, and analysed. It was found that considerable decomposition had occurred into carbon monoxide and oxygen, $2CO_2=2CO+O_2$. A series of experiments gave the following results:—When carbon dioxide at 5 m.m. pressure is sparked in an ordinary vaccum tube for ten minutes, 63 per cent of the gas is decomposed, and when sparked for 5, 3, 2½, 1, and even ½ a minute, as much as 58—60 per cent decomposition occurs. In fifteen seconds one experiment showed that 48 per cent was decomposed, whilst in some others when the gas was sparked for ten seconds at 10, 3, and 1 m.m. pressure, 32, 55, and 65 per cent respectively was decomposed. Most of these experiments were made with platinum electrodes. Aluminium electrodes gave a rather higher amount of decomposition, whilst with an electrodeless tube only 50 per cent suffered decomposition after one minute sparking.

Another interesting observation was that if the platinum electrodes are allowed to become red-hot, re-combination at once occurs between the carbon monoxide and oxygen till the gas which remains, instead of containing the products of decomposition of 60 to 70 per cent of the carbon dioxide, is almost pure carbon dioxide.

Under electrical strain, therefore, at low pressures, carbon dioxide is a very unstable gas, but when the products of decomposition come in contact with red-hot platinum wire re-combination occurs. Carbon monoxide, even after twenty minutes' sparking, seemed almost unchanged, and gave only a faint turbidity with baryta water. When a mixture of carbon dioxide and hydrogen is sparked at reduced pressures small quantities of a gas, which seems to be methane, are formed, but under no conditions could formaldehyde be detected. It is probable that the methane is formed by the action of hydrogen on carbon monoxide.

*112. "*Halogen Derivatives of* p-*Cymene from Substituted Nitro-Camphanes.*" By M. O. Forster and W. Robertson.

The oil which accompanies the conversion of 1 : 1-bromonitrocamphane into the anhydride has been identified as bromo-*p*-cymene [$CH_3 : Br : C_3H_7\beta = 1 : 2 : 4$].

The *anhydride* of 1 : 1-chloronitrocamphane, prepared by dissolving that substance in cold concentrated sulphuric acid, crystallises from alcohol in colourless opaque prisms, and melts at about 230°; chloro-*p*-cymene is formed during the production of this compound. The *isomeride*, $C_{10}H_{14}ONCl$, obtained by the action of an alcoholic solution of hydrochloric acid, crystallises in transparent, six-sided plates, and melts at 248°; it forms a *benzoyl* derivative, which melts at 166°.

The *hydroxylamino*-derivative, $C_{10}H_{17}O_2N_2Cl$, prepared from either compound by the action of alcoholic hydroxylamine, melts at 187°; the *benzoyl* compound melts at 164°.

The *nitro*-derivative of the anhydride melting at 248° crystallises in flat prisms, which melt at 71—72°; reduction with zinc and acetic acid regenerates the anhydride.

113. "*On a Theory of Chemical Combination.*" By G. MARTIN.

Atoms are complex structures analogous to a benzene nucleus which in their ordinary state are incapable of acting on each other, but if by some cause the atomic ring is broken, the atoms become capable of acting together. In this state they are said to be "ionised." Chemical action will only take place of its own accord when the rate of variation of ether strain experienced by a molecule, produced by the approach and recedence of neighbouring molecules, is of such a rate as to coincide with an internal rate of vibration of an atom or molecule. The atoms thus become ionised. The dissociation of gaseous molecules is controlled by two circumstances:—(*a*) The gradual increase of temperature, by increasing the velocity of the atoms in the molecule, may cause it to decompose of its own accord; (*b*) if the rate of vibration of ether strain happens to coincide with the rate of vibration of the molecule, the dissociation will occur long before cause (*a*) of itself would cause decomposition.

In dissociation the atoms need not necessarily be ionised. The rapid increase of velocity of reaction with the temperature is due to the coincidence of the time rates of atomic vibration, and the rate of variation of ether strain.

If two gaseous molecules, *A* and *B*, act on each other at (say) t°, then the same reaction will also take place at higher temperatures—t'° and t''°—the condition being that at t° the rate of variation of ether strain is approximately equal in value to the rate of vibration of the atoms of the molecule. But at t'° and t''° the rate of variation of ether strain is respectively double or treble the rate of atomic vibration. It may happen, however, that the products of the change are incapable of existing at these temperatures. The atoms will, however be ionised at each of the ranges t°, t'°, and t''°, no matter whether any reaction takes place or not. At intermediate temperatures no reaction will take place. In certain cases we have experimental evidence of such ranges of temperature, silicon hexachloride, Si_2Cl_6, for example, is stable enough at the ordinary temperature, but above 300° its vapour begins to dissociate, and at 800° it is entirely decomposed. If, however, the temperature be raised rapidly above 1000° no decomposition of the substance occurs. The substance, therefore, is stable above 1000° and below 350°, but will not exist at intermediate temperatures.

The occurrence of these temperature ranges may be obscured by the fact that the products of the reaction may exist continuously from one range to the other.

A reaction will only proceed to completion when the rate of variation of ether strain necessary to cause the molecules to react together does not also induce the products of the change to decompose. Complete reactions occur only very seldom, as a complex molecule has so many modes of vibration that it is not difficult for it to be affected at almost any temperature.

114. "*On the Occurrence of Paraffins in the Leaf of Tobacco.*" By T. E. THORPE, C.B., F.R.S., and J. HOLMES.

In connection with the working of the Revenue Act, which imposes a limit upon the amount of oil which may be present in manufactured tobacco, the authors have had occasion to study the nature of the material which is extracted from tobacco by "petroleum-ether." In the extract thus obtained, they have discovered the presence of two paraffins, *hentriacontane*, $C_{31}H_{64}$, melting at 67·8—68·5°, and *heptacosane*, $C_{27}H_{56}$, melting at 59·3—59·8°, which are present in the leaf in about equal amounts to the extent, in the aggregate, of rather more than 1 part per 1000.

In Kentucky and Virginia leaf, the mixed hydrocarbons, in three separate preparations, had the following melting-points:—Western leaf, 63·0—63·8°; "wrappers," 63·5—64·0°; "fillers," 63·7—65·0°. The authors are of opinion that the snow-white substance of satiny lustre extracted from Kentucky tobacco by Kissling (*Ber.*, 1883, xvi., 2432), which he found to melt at 63·0°, and which he regarded as probably an impure mellissyl mellisate, and the substance of similar appearance found by him among the constituents of tobacco-smoke, melting at 64·5°, but which he regarded as a hydrocarbon, are in reality the same products, and identical with the mixture of the two paraffins, the heptacosane, $C_{27}H_{56}$, and hentriacontane, $C_{31}H_{64}$, of Krafft, which the authors have found to be present in all the American tobaccos examined by them.

115. "*Two New Substances in Lemon Oil.*" By H. E. BURGESS.

If 3 or 4 litres of the terpenes obtained during the distillation of the lemon oil are well shaken with a cold solution of sodium metabisulphite, a small quantity of a crystalline compound is formed which can be separated and washed with alcohol and ether. This on being decomposed in the usual way gives an aldehyde of which the constants are very different from those of citral:—Boiling-point, 80—85° at 15 m.m.; optical rotation, +0° 30′; refractive index, 1·4314 at 20°.

It has an odour resembling cocoanut oil. On shaking the aldehyde with hydrogen peroxide and caustic soda solution it is at once polymerised into a solid form which can be re-crystallised from alcohol.

It forms an oxime melting at 35°, and on oxidation with potassium permanganate it gives an oily acid; from the ammonium salt the silver, copper, and magnesium salts have been prepared and analysed.

Apparently the same aldehyde exists in orange oil, but was not found in the terpenes as in the case of lemon oil.

A crystalline substance was obtained by shaking together 1 litre each of acetone and lemon oil, and then adding about 200 c.c. of water, when it separates into two layers; the lower portion was separated, and allowed to stand for twenty-four hours, when small crystals were formed in the globules of oil floating on the surface; these were filtered off, and re-crystallised from alcohol and ether.

Several such separations may be made from each quantity of oil, but the total yield from 1 litre was extremely small. The crystals so obtained melted at 145°. They are sparingly soluble in alcohol, the solution having a marked blue fluorescence.

Several combustions have been made of the re-crystallised substance which forms a crystalline dibromide, and is oxidised to oxalic acid and carbonic acid.

116. "*Preparation and Properties of* 2 : 6-*Diketo*-4-*isopropylhexamethylene* (2 : 6 · *Dihydroxy* · 4 · *isopropyldihydroresorcinol*)." By A. W. CROSSLEY.

Ethyl 2 : 6-*diketo*-4-*isopropylhexamethylene* · 3 · *carboxylate*, obtained by the condensation of *iso*butylideneacetone and ethyl malonate, separates from a mixture of benzene and light petroleum in small needles melting at 101°. When boiled with sodium carbonate or potassium hydroxide solution it yields:—

2 : 6-*Diketo*-4-*isopropylhexamethylene*,—

$$C_3H_7HC\begin{<}CH_2\cdot CO\\CH_2\cdot CO\end{>}CH_2,$$

which crystallises from dilute alcohol, with $1H_2O$, in well formed needles, melting at 67·5°. Its constitution is proved by its method of formation, and because on oxidation with sodium hypobromite it yields *β-iso*propylglutaric acid. The *silver* salt is an insoluble white precipitate, and the *dioxime* separates from dilute methyl alcohol in clusters of stumpy needles, melting somewhat indefinitely about 145°.

When hydrolysed with barium hydroxide diketo*iso*propylhexamethylene is converted quantitatively into *β*-iso*propyl*-*γ*-*acetylbutyric acid*,—

$$C_3H_7C\begin{cases}H\\ <\end{cases}\begin{matrix}CH_2\cdot CO_2H\\ CH_2\cdot CO\cdot CH_3\end{matrix}$$

which is an almost colourless oil, boiling at 195° (39 m.m).

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, June 28th, 1901.

Prof. Everett, Vice-President, in the Chair.

This meeting, by invitation of Prof. W. G. Adams, was held in the Wheatstone Laboratory, King's College.

A paper on "*The Effect of a High Frequency Oscillatory Field on Electrical Resistance*" was read by Mr. S. A. F. White.

The object of this paper is to discover if the action of light upon the electrical resistance of selenium can be imitated by using high frequency electrical oscillations. It is found that such oscillations permanently increase the resistance of selenium. The effect of a rise of temperature is to increase the resistance of a piece of low resistance, and decrease the resistance of a piece of high resistance. The effects of the field on a piece of high resistance can be reversed by exposure to light or by re-heating and subsequent cooling. In the case of tellurium a high frequency field temporarily decreases the resistance, as also does a rise in temperature. Repeated heating and cooling of a piece of tellurium permanently increases its resistance. It seems probable that all of the effects are due to rise of temperature caused by minute sparks within the mass. The rise in resistance by alternate heating and cooling may be due to the formation of tellurides with the metal of the electrodes. The large negative temperature effect of tellurium suggests that it might be usefully employed in the detection of heat radiation.

The Chairman expressed his interest in the paper, and drew attention to the very rapid action of light upon selenium.

Prof. Adams said that as the effects here noticed were not so rapid as in the case of light they were probably due to change in temperature.

Prof. Bose said he had tried the effect of Hertzian radiation upon thin layers of various metals, and found an increase of resistance in the case of selenium and a decrease in the case of tellurium. The effect of radiation is confined to a few layers on the surface of the conductor, but it appears that it is of the same nature in continuous solids as in coherers.

A paper by Mr. E. C. C. Baly and Dr. H. W. Syers, on "*The Spectrum of Cyanogen*," was read by Mr. Baly.

The authors have been able to obtain the spectrum of cyanogen by allowing the pure gas to flow through a vacuum tube, and observing from the end of the tube. This is necessary on account of the brown deposit of paracyanogen which renders observation in the ordinary way impossible. The spectrum obtained differs from the flame spectrum, and consists of a series of equidistant flutings through the whole of the red and yellow—somewhat recalling those of the positive band spectrum of nitrogen. The experiments prove that (1) the Swan spectrum is not produced by a carbon compound which does not contain oxygen; (2) the Swan spectrum is that of an oxide of carbon, as it is only produced by carbon monoxide; and as this spectrum is changed at once into the carbon oxide spectrum by admission of oxygen or by intense electric discharge; and further, as the carbon oxide spectrum is invariably given by carbon dioxide there can be no doubt that (3) the Swan spectrum is that of carbon monoxide, and the carbon oxide spectrum that of carbon dioxide.

Mr. Gaster said that this paper might throw light on the discussion of the arc where cyanogen, carbon monoxide, and carbon dioxide are present. The presence of cyanogen might be able to explain the hissing of the arc.

The Society then adjourned until next October.

CORRESPONDENCE.

ESTIMATION OF AMMONIA IN ITS SALTS.

To the Editor of the Chemical News.

Sir,—However original Mr. Bennett Blackler's process may be, and however accurate it may be in the case of pure ammoniacal salts—which, knowing beforehand that they are pure, there is no necessity to analyse—it must of necessity fail in the case of a complete analysis of commercial sulphate of ammonia, such, for instance, as put in the market by the London and provincial gas companies, or in a mixture of superphosphate of lime and sulphate of ammonia, to say nothing of acid and basic phosphates of ammonia and mixtures thereof.

Let Mr. Blackler estimate in a commercial sample of sulphate the *free acid*, the moisture, the insoluble, the ammonia as determined by this method, and the total sulphuric acid, together with the nitrogen existing in other combinations than sulphate, and see whether, even after making allowance for free acid, his figures do not total considerably over 100.

The complete analysis of commercial sulphate is not done by a magic wand process. Let Mr. Blackler fill up the following blank form from his results after having made the corresponding determinations on an actual commercial sample:—

	Per cent.
Moisture	—
Free sulphuric acid	—
Combined sulphuric acid	—
Ammonia as determined by Mr. Blackler's process:—	
1. (NH_3) equivalent to combined sulphuric acid	—
2. Excess of ammonia over that required to saturate combined H_2SO_4 after deducting the excess of ammonia due to free acid and which in his process is estimated as sulphate of ammonia ..	—
Insoluble organic matter	—
Insoluble inorganic matter	—

Again, unless an ash determination were made, it would be quite possible to fake up sulphate, &c., of ammonia most grossly with acid sulphate of soda if this process were relied on solely.—I am, &c.,

J. G. McIntosh.

AMERICAN *v.* ENGLISH SPELLING.

To the Editor of the Chemical News.

Sir,—The recent correspondence in the Chemical News anent American *v.* English spelling of chemical terms impels me to give a brief history of the "rules" which have been several times referred to.

In view of the variable usage in the pronunciation, and to a lesser extent in the spelling, of chemical terms, the Chemical Section of the American Association for the Advancement of Science appointed a committee at the New York meeting in 1887 to take the subject under consideration. This committee consisted of Prof. Thomas H. Norton, of the University of Cincinnati, Dr. H. Carrington Bolton, of Washington, and Prof. Edward Hart, of Lafayette College. An informal report was made

at the Cleveland meeting the next year, and the committee was continued; at that time I was added to the committee, and acted as its secretary.

In May, 1889, quite a long list of words, the spelling or pronunciation of which might be considered doubtful, was widely distributed among American chemists. Based on the replies received, a report was made to the section at the Toronto meeting, and fully discussed. At that meeting the committee of the Section was made a special committee of the Association. The report of this year was printed and distributed with requests for criticism. The third report of the committee was read and discussed at the Indianapolis meeting in 1890. On a large proportion of the words substantial agreement had been reached, and a list of the remainder was for the third time sent out. The fourth and final report of the committee was adopted by the Chemical Section at the Washington meeting in 1891, and afterwards by the Association. It was also reprinted in chart form by the Bureau of Education, and distributed to secondary schools all over the country. The printed reports and references to the committee will be found in the *Proceedings* of the Association as follows:—1888, p. 131; 1889, pp. 186—194, 478; 1890, pp. 150—158; 1891. pp. 173—178; 1893, p. 366.

The fact that there was great divergence in usage in this country seemed to call for the appointment of such a committee; the sole aim of the committee was to secure if possible a uniform usage; to this end the co-operation of chemists generally was sought. The original list and the three successive reports were sent to every American chemist whose address could be secured, with urgent requests for full comment and criticism. Several attempts were also made to secure the co-operation of English chemists, but I think I am not in error in stating that no notice was taken of these requests. It may be added that every doubtful point was submitted not only to chemists, but to a number of philologists.

That the work of this committee has not been successful in harmonising even American usage must be admitted. Many writers follow the recommendations of the final report; more do not. Those who have criticised the final report most freely are those who refused all co-operation while the work of the committee was in progress.

Perhaps I may add that in only two instances did the Chemical Section reverse the views of the committee. The committee favoured "sulphur," even though as high an authority as Professor March considered "sulfur" to be correct, and a majority of the committee favoured "aluminium" rather than "aluminum," but commercial usage had so popularised the latter form that the committee was reversed.—I am, &c.,

JAS. LEWIS HOWE.

Washington and Lee University,
Lexington, Va., June 7, 1901.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxii., No. 23, June 10, 1901.

Neutralisation. Titration of Acids and Alkalis of Complex Function.—M. Berthelot.—Complex functions of acids and alkalis can be detected, and even estimated to a certain extent, by various colouring-matters. The number of indicators apt to vary under the action of acids or alkalis being considerable, and the amount of divergence varying for each one, according to the conditions of equilibrium which determine the functions of the acids or alkalis producing the divergence, the author limits himself to the indicators tournesol, methyl-orange, and phenolphthalein. With these he experiments on acid-alkalis derived from the acid alcohol, *e.g.*, glycocoll, &c., the three oxybenzamic acid isomers, and hippuric acid, the normal amido-derivative of oxyacetamine and benzoic acid.

Experimental Verification of a Law of Mechanical Chemistry.—H. Pélabon.—The action of hydrogen on mercury sulphide, and the inverse reaction of sulphuretted hydrogen gas on mercury, leads to the investigation of a system containing four volatile bodies,—

$$\underset{1}{HgS} + \underset{2}{H_2} = \underset{3}{H_2S} + \underset{4}{Hg}.$$

Using the indices 1, 2, 3, 4 respectively for the four bodies, it is easily seen that the general relation existing between the partial pressures of the gases and vapours contained in the system is of the form—

$$\log \frac{p_1^{2v}\, p_2^{2v}}{p_3^{2v}\, p_4^{2v}} = F(T);$$

$2v$ is the volume occupied by all the molecules of the simple and compound bodies. If any of the pressures become zero, the expression is simplified into—

$$\frac{p_1 p_2}{p_3 p_4} = f(T).$$

The author submits this formula to an experimental verification.

Action of a Metallic Hydrate on Solutions of Salts of other Metals. Basic Salts containing Two Metals.—A. Recoura.—The author's experiments verify those results already published on the action of metallic chlorides, and show that in reactions in which $4CuO$ plays a part, and which reappear so frequently in the history of the copper compounds. He has compared them together in the form of a table, giving in each case the quantities of the various sulphates which combine with $4CuO$. The compounds not being crystalline, the water of combination was not determined. In all cases it was found that cupric hydrate combines with the same quantity of all the sulphates examined, with the exception of nickel, to give the compound $3CuO(MOSO_3)$, corresponding to the sulphate, $3CuO(CuOSO_3)$; the latter substance being formed when hydrate of copper comes in contact with a solution of copper sulphate.

The Imidodithiocarbonic Ethers, $RN=C(SR')_2$.—Marcel Delépine.—The author's experiments on the imidodithiocarbonic ethers give results confirming the formulæ and reactions previously admitted. The details of analysis on which they are based were published at the same time as the individual investigation of the ether in question. Thanks to the new method of preparation, in which the yield is considerable, the author hopes to be able to continue his research and extend it to the derivatives of the thiosulphocarbamates of the secondary amines, which substances react very easily on the alcoholic iodides, and in a similar manner to that which he discovered with regard to several fatty amines and piperidine.

Active Erythrites.—L. Maquenne and G. Bertrand.—In two previous papers, the authors announced the existence of two active tetrites, predicted by theory, and described their principal characteristics. These two substances, called *l*-erythrite and *d*-erythrite, are now studied more carefully, and, having completed their chemical history, all previous predicted properties were verified. The results also show that these two substances represent the optical antipodes of active erythrite; that which is formed during the hydrogenation of erythrulose corresponding to ordinary tartaric acid, whilst the other corresponds to lævo-tartaric acid, and, in consequence, ought to have a place by the side of this in the left series.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxv., No. 3.

Action of Hydrogen on Protosulphide of Bismuth.—H. Pélabon.—Already noticed.

The Double Chlorides of Uranyl and the Alkaline Metals; and the Hydrochlorate of Choride of Uranyl.—J. Aloy.—Already inserted in full.

On Oxide of Bismuth.—P. Thibault.—Already inserted in full.

Specific Molecular Heat of Dissociable Gaseous Compounds.—M. Ponsot.—Already noticed.

The Complex Salts of Platinum. (IV.). Alkalino-earthy Oxalonitrites.—M. Vèzes.—Already inserted in full.

The Dialcoylamido-ortho-benzoylbenzoic Acids and their Derivatives.—A. Haller and A. Guyot.—Following on their previous researches on the preparation of these acids, the authors have now examined the preparation and properties of some of their derivatives. The dialcoylparamido-orthobenzoylbenzoic acids are obtained by the condensation of equal molecules of phthalic anhydride and a tertiary aniline of which the para-position is not occupied. For this reaction to take place, it is, as a rule, necessary to use a condensation agent, such as $AlCl_3$. Dimethylamidobenzoylbenzoic acid is easily obtained in the pure state, with a return of 75 per cent of theory, by the condensation of phthalic anhydride and dimethylaniline in the presence of chloride of aluminium. It occurs in bright yellow prisms, fusible at about 202—203°, having a very sweet taste and almost insoluble in water, ether, benzine, toluene, and chloroform, but very soluble in hot methylic and ethylic alcohol, from which they crystallise on cooling with or without a molecule of alcohol of crystallisation. Diethylamidobenzoylbenzoic acid is prepared in exactly the same manner as its lower homologue, but replacing the dimethylaniline by diethylaniline. It has analogous properties, it fuses at 180°, and is very sweet to the taste. Ethylbenzylamidobenzoylbenzoic acid is obtained in a similar manner to its lower homologues by the condensation of ethylbenzylaniline with phthalic anhydride in the presence of chloride of aluminium. The detailed preparation of this acid is given, as it differs in some important particulars from that of the others.

No. 4.

The Blue Oxide of Molybdenum.—Marcel Guichard.—Already noticed.

The Action of Water on Pentachloride of Molybdenum.—Marcel Guichard.—Already inserted in full.

Action of Bromide of Aluminium on some Acyclic Chlorised Hydrocarbides.—Ch. Pouret.—By the action of powdered aluminium on the perchlorised derivatives CCl_4, C_2Cl_4, and C_2Cl_6 in the presence of bromine, the author has in every case obtained hexabromethane, C_2Br_6, and at the same time some resins. He now fully describes the preparation of bromoform, bromide of methylene, and bromide of methyl.

Thermic Data relative to Orthomonochlorobenzoic Acid.—G. Massol.—The heat of formation of the ammoniacal salt has been found to be lower than that of benzoate of ammonia. Again, the heat of formation of the potash salt with half a molecule of water was found to be equal to that of benzoate of potash, but it is evident that the anhydrous salt would give off a slightly greater amount of heat. Orthomonochlorobenzoate of soda gave a heat of formation higher than that of the benzoate of soda.

Thermic Data relative to Orthomonoiodobenzoic Acid.—G. Massol.—This acid is too slightly soluble in water to allow of its heat of solution being determined directly. Its heat of neutralisation is—

$C_7H_5IO_2$ sol. + NaOH diss. =
$= C_7H_4IONa$ diss. . . . +9·48 cal.

The anhydrous salt was obtained after prolonged desiccation at 120°; its heat of solution in water is +2·96 cal. at 12° C. for 1 molecule (molecular weight = 270) in 4 litres.

The Cyclic β-Diketones.—Georges Leser.—Already noticed.

Preparation and Properties of Dialcoylamidoanthraquinones.—A. Haller and A. Guyot.—A long paper, not suitable for useful abstraction.

On some New Colouring-matters.—E. Grimaux and Leon Lefèvre.—Colours derived from triphenylmethane and its homologues are dinitrated and then acted upon, according to the known methods, by phenols, naphthols, or amines. In this manner, triamines, diamines, or monoamines were operated upon, and new colours produced.

Blue Colouring Materials derived from Triphenylmethane.—E. Grimaux.

Rose Colouring Materials derived from Triphenylmethane.—E. Grimaux.

Derivatives of Triphenylmethane.—E. Grimaux.

Preparation of Alkylised Meta-amino-phenols.—E. Grimaux.

The Colouring Materials derived from the Dialkylised Meta-amino-phenol Ethers.—E. Grimaux.—The above five papers all briefly describe the author's experiments and the preparation and properties of the materials referred to.

The presence of Oxysulphocarbonate of Iron in the Waters of the Rhone.—H. Causse.—Already noticed.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 1st inst., His Grace the Duke of Northumberland, K.G., President, in the Chair. Mr. A. C. Allen was elected a Member.

Institute of Chemistry of Great Britain and Ireland.—*The Final Examination for the Associateship in the Branch of Biological Chemistry.*—An Examination in this Branch will be held at the Laboratories of the Institute, 30, Bloomsbury Square, London, W.C., in October next. The exact date will be communicated to intending candidates. Candidates desirous of presenting themselves are required to notify the Registrar on or before Tuesday, the 3rd day of September, 1901. The Examination is open to any candidate whose application for admission to the Final Examination has been accepted by the Council, and any candidate who has passed the Intermediate Examination of the Institute. The Examination will extend over at least four days, and may be theoretical, practical, written, and oral, and the syllabus will include the following:—Biological Chemistry, with special reference to the chemistry and bacteriology of foods, water, sewage, and effluents, and the practical applications of Biological Chemistry to industries. Examinations in the branch of Biological Chemistry of the Final Examination will be held annually in October, while the Examinations in the other branches will be held in January and July as heretofore. Candidates intending to enter for the Final Examination in the branch of Biological Chemistry are recommended to take (after passing the Intermediate Examination, or any examination qualifying for admission to the Final) a course of study covering the following work:—A course of 40 to 50 lectures on the Morphology and Physiology of Micro-organisms. Practical work to include—(*a*) Microscopy, the preparation, staining, mounting, drawing, and recognition of specimens; (*b*) the preparation and study of pure cultures; (*c*) the conduct of fermentation experiments and the study of chemical changes brought about by bacteria, moulds, yeast, &c.

THE CHEMICAL NEWS.

VOL. LXXXIV., No. 2172.

A NEW TEST FOR CHLORINE FOR USE WITH THE BLOWPIPE.

By HENRY W. NICHOLS.

A PIECE of absorbent paper moistened with a solution of cobalt chloride turns blue when warmed.

A piece of absorbent paper moistened with a solution of cobalt bromide or iodide turns green when warmed.

A piece of absorbent paper moistened with a solution of cobalt nitrate turns a deeper rose colour and darkens when warmed.

Paper moistened with solutions of other cobalt salts, when dried in the air, does not turn either green or blue at a temperature below that of the carbonisation of the paper.

Paper moistened with a solution of cobalt nitrate and a soluble chloride acts upon warming as if it were moistened with cobalt chloride.

Upon these facts is based the following tests for chlorine and for the distinction between chlorine and bromine or iodine. This test calls for such apparatus and reagents only as are commonly used in blowpipe work:—

Powder the assay with from one to four volumes of potassium bisulphate. Place the mixture in a closed tube. Moisten a fragment of filter-paper with cobalt nitrate solution and place it in the mouth of the tube. Upon fusing the mixture, the paper under the influence of the hydrochloric acid and sulphuric anhydride given off will turn a bright blue if chlorides are present. If bromides or iodides are present the colour will be green. In case of minute quantities it may be necessary to dry the paper before the colour appears, but ordinarily the sulphuric anhydride evolved by the bisulphate produces the same effect as heating. Although the blue of the cobalt chloride assumes, when faint, a greenish cast, yet it is always distinct from the yellowish-green of bromides. When chlorides and bromides are found together, the paper turns first blue from chlorine and later green from bromine. If but little bromine is present the final colour will be a bluish green. The test is much less delicate for bromides than for chlorides. If but little chlorine is present and much water condenses in the tube, this water may hold back the hydrochloric acid and should be driven into the test paper. When this occurs it is often necessary to heat the paper to bring out the colour, and under these conditions the yellow of the charred paper may produce with the blue a green, somewhat similar to that produced by bromides. Acid potassium sulphate, as purchased, contains too much sulphuric acid and should be fused in platinum until frothing ceases before use; otherwise it froths in the tube in a disagreeable manner. Many bromides contain sufficient chlorine to give a distinct test by this method, a fact that should be remembered when using them for check experiments. The limit of sensitiveness of the test has not been determined. The following tests will indicate its suitability for blowpipe work and mineral determinations: two specimens of embolite were tested and both the chlorine and bromine were indicated. A specimen of sodalite (Cl, 7·3 per cent) gave a good reaction for chlorine, as did a specimen of zunyite (Cl, 2·91 per cent) with about 25 per cent of gangue. The white crystalline apatite of Snarum, Norway, gave a good reaction, while a specimen of the green massive Canadian apatite gave no reaction for the traces (0—0·5 per cent) it generally carries.

Chlorides in solution may be tested by dipping a paper into the solution, spreading a drop of cobalt nitrate solution upon it, drying, and heating. The test thus carried out is not very delicate; moreover, the distinction between chlorides and bromides is obscured, and sulphides and some other substances interfere.

The familiar test for chlorine in the presence of bromine by the generation of chlorochromic anhydride may be advantageously modified for the blowpipe laboratory. In place of the tubulated test-tube a plain test-tube may be used, and in place of the receiver a piece of filter-paper moistened with a saturated solution of sodium carbonate and placed in the mouth of the tube. This alkaline paper retains chromic acid, so that when burned in the forceps the ash will give a chromium reaction with the borax bead. No difficulty will be found in burning the paper while moist, owing to the bromates and chromates present. During the burning the sodium carbonate fuses and collects the ash into a globule which will be a dirty green if it contains much chromium. For the small quantities of material commonly used in mineral testing, a closed tube may be very advantageously substituted for the test-tube whenever the substance tested does not effervesce with acid.—*American Chemical Journal*, XXV., No. 4.

NOTES ON SOME BLOWPIPE TESTS.

By JOSEPH W. RICHARDS.

Closed Tube Test.—This test may easily be made quantitative for approximate determinations of water, volatile sulphur, &c. A weighed amount of material is put into the tube, tapped down, and heated regularly. The upper part of the tube containing the sublimate is then nicked with a file and broken off. If water is being determined, two small corks are put into its ends, to prevent evaporation. The piece of tube and sublimate are then weighed; then the tube is heated until the sublimate is driven off, and weighed again. The results on pyritic ores have proved satisfactory. A piece of göthite gave 10·28 per cent water; theory requires 10·11 per cent. Time, five minutes.

Open Tube Test.—The behaviour of the antimony coat is sometimes different from that usually described in the books. The entirely volatile oxide, Sb_2O_3, is sometimes the only product, not a trace of the non-volatile Sb_2O_4 being formed. I have observed this in allemontite, dyscrasite, and ullmannite, particularly. It takes nearly a red heat to volatilise this coating, and if the upper end of the tube from which the vapours are escaping be held in the flame, the latter is coloured pale yellowish green (arsenic, pale blue). Penfield is the only writer who mentions the formation of this volatile coating exclusively by some minerals, but his experience as to which give it does not exactly coincide with mine.

It is important when testing in the open tube, if any substance whatever does not give a sublimate in lump, to powder it, and finally to heat with the blowpipe flame from the outside as hot as the glass will stand. Some sulphides, such as sphalerite and argentite, do not roast until thus heated. With these precautions the test is uniformly reliable.

Flame Tests.—When testing for phosphoric acid, the assay on platinum wire is touched when *hot* to concentrated sulphuric acid, and brought into the outside edge of the Bunsen flame as *low down* as possible, and as slowly as possible. By thus proceeding, phosphorus can be infallibly detected in any combination, according to my experience, thus rendering unnecessary the ammonium molybdate test. The flame is slightly bluish green close to the wire, greyish green a short distance away, and yellowish green farther off.

When testing similarly for boron, the assay should be held slightly higher, say an inch higher, in a hotter part of the flame. When testing for boron with Turner's mixture, it is an advantage to moisten the mass to a paste

with a drop of concentrated sulphuric acid, and then put moist into the edge of the flame.

Reduction to Metal.—When reducing with soda on charcoal, if an assay proves very refractory, it is uniformly of advantage, and never deleterious, to add some borax to the assay. This is particularly useful in reducing tin oxide, and is to be preferred to potassium cyanide because of its harmlessness.

Test for Fluorine.—The fusion with potassium bisulphate decomposes any fluoride, but the test of the vapours with Brazil wood paper is not reliable. Light, air, and age seem to deteriorate rapidly the sensitiveness of the paper. I have found it more reliable to make the fusion in a rather large closed tube, of say 5 to 8 m.m. diameter, heating regularly with the tube almost horizontal. The silica ring deposits just above the assay, and the odour of the gas is often quite plain, Cool the tube, nick it below the silica ring, break, and hold the upper end vertically under and close to the nose. At this instant the odour of hydrofluoric acid will be perceived with certainty, if any has been driven off, and by a little experience the odour can be distinguished with as much certainty as the smell of ammonia. A still more conclusive proof consists in letting water run slowly over the silica ring. If it is merely a sublimate of a volatile salt, it will be dissolved and disappear; if it is the true silica ring, it will become gelatinous, seen under the lens, and on carefully drying the tube the white ring is again strongly in evidence.

Test for Arsenates.—All give the arsenic odour and coat on charcoal, but sometimes so slowly as easily to escape detection. Mixing with charcoal dust and soda, and fusing in the closed tube or open tube does not invariably give metallic arsenic or the oxide, on account of the heat being insufficient to reduce some arsenates, *e. g.*, of zinc. Putting this mixture in the lower end of an open tube, and playing on it with the reducing flame of the blowpipe directed into the tube, will always give the arsenic coating. All mercury compounds are also thus reduced, and deposit a mercury coating, and it is a good means of testing for antimonates, tellurates, and selenates, while ammonium compounds give ammonia gas.

Test for Silica in the S. Ph. Bead.—Many silicates are attacked rapidly, the bases dissolved, and the silica left either in flocks or as a skeleton. However, on long blowing, some silica dissolves in the bead, and if only a small piece of mineral is used and the blowing is strong, all may dissolve up clear. Hirschwald determined that the bead can dissolve 2·5 per cent of its weight of silica; my tests have shown close to 2 per cent, but that more can be dissolved if other bases are present. For instance, the bead dissolves—

Per cent of silica.

2·25	if no other base is present,
2·25	3·85 per cent of alumina is present,
3·03	8·52 „ „ lime „ „
3·40	3·17 „ „ „ „ „
4·04	10·91 „ „ zinc oxide is present.

It results from this behaviour, that in silicates rich in bases, an amount of mineral equal to even 30 per cent of the weight of the bead (as in thaumasite) may be dissolved up clear. Two observations will obviate this difficulty. If the mineral is not white, as it is attacked, the edges will become white and clear as it is being dissolved, and the presence of silica thus proved. If the piece is white or clear, the blowing must be interrupted several times, and then with the lens the silica can be recognised floating in the bead. If the bead is clear, a further addition of a lump, say one-third the size of the bead, will always, on further blowing, cause the opalescent milkiness due to silica. By attending to these points, I think that silica can be found with certainty in all these silicates which are easily decomposed.

A different case is presented by those silicates which are attacked slowly and dissolve *en masse*, without showing a skeleton. They are not numerous, and are principally the silicates of aluminium, glucinum, or zirconium. In such cases, by long blowing (five minutes), enough silica is usually dissolved in a small bead to make it milky opalescent, which silica alone produces when present in such a small amount as even less than three per cent. The presence of silica can thus be proved. The minerals which dissolve slowly in salt of phosphorus and do not contain silica are principally corundum, diaspore, chrysoberyl, cassiterite, spinel, chromite, gahnite, and xenotime. They should be brought to mind and kept in consideration in connection with such few silicates as dissolve very slowly like the above.—*Journal of the American Chemical Society*, xxiii., No. 4.

ON TRIPHENYLCHLORMETHANE.

By M. GOMBERG.

THE recent publication by Norris and Sanders (*Am. Chem. Journ.*, xxv., 54) on the same subject induces me to make a few remarks at this time. It is far from my intention to enter into any controversy whatever. I merely wish to call attention to the following few points:—

(1) My paper on "Triphenylchlormethane" (*Journ. Am. Chem. Soc.*, xxii., 752) was first presented by me at the Columbus Meeting of the American Association for the Advancement of Science, August, 1899. Norris and Sanders state that they have been at work on this subject for about a year. Hence this subject must have been undertaken by them after my paper was presented. It was, however, entirely natural that they should have overlooked the first mention of my paper, since it was given in the Proceedings (*Proceedings American Association for the Advancement of Science*, 1899, xlviii., 152) only by title.

(2) The difference in procedure between my method and that of Norris and Sanders consists in that the latter used, instead of benzene as a solvent, carbon disulphide—a diluent first introduced by Anschütz (*Ann. Chem. Liebig*, ccxxxv., 341) for Friedel and Crafts' reaction in general. The application of this solvent in the present instance enabled Norris and Sanders to isolate the important intermediate product, the double salt of aluminium chloride and triphenylchlormethane, which was not obtained by me at all.

(3) Norris and Sanders state (*loc. cit.*, p. 59) that the action of sodium upon triphenylchlormethane is entirely negative, even on two weeks' contact in ether. Only on the addition of brombenzene to the above mixture did a reaction take place. One of the several products was a body free from halogen, yet on analysis the carbon and hydrogen did not add up to 100 per cent. The fact that "this compound resembles closely in melting-point, chemical composition, and solubility" the substance (the peroxide) described by me (*Journ. Am. Chem. Soc.*, xxii., 762) shows that it is an oxygen body. One fails to see, however, how Norris and Sanders "discovered that an oxygen compound was formed as the result of the action of sodium on a mixture of triphenylchlormethane and brombenzene." No evidence is given that they excluded all oxygen-carrying reagents, such as sodium oxide, and that this was not the cause of the formation of that body, or that they worked in an atmosphere free from oxygen, and in this way established the non-formation of that body under these conditions. Furthermore, if the substance is really identical with the peroxide mentioned, it is not the result of the action of sodium upon a mixture of the two halogen compounds, but is formed by action of the atmospheric oxygen upon the unsaturated hydrocarbon (triphenylmethyl) which must have resulted in some way from the action of sodium upon triphenylchlormethane alone. (Experiments show that small quantities of the triphenylmethyl *are* produced in this way). The reaction must, therefore, be analogous to that described by me for

other metals: silver, zinc, and mercury. Only these three metals, in addition to the unsatisfactory results with sodium, are mentioned in my preliminary paper. Other metals, however, and different solvents, have also been tried and are being studied at present. Norris and Sanders now "propose to investigate the action of sodium on ethereal solutions of triphenylchlormethane of varying concentrations." I regret that having cleared up the difficult part of the problem (the action of metals upon triphenylhalogenmethanes) I am not to have, as it appears from Norris's publication, this field to myself for a while longer. It was stated (*Journ. Am. Chem. Soc.*, xxii., 776) in my preliminary paper that only about two-thirds of the theoretical quantity of the unsaturated hydrocarbon is formed. The nature of the other products is being studied, and I find that this varies according to the metal and solvent employed.—*Journal of the American Chemical Society*, xxiii., No. 2.

ON THE IMPORTANCE OF FORMIC ALDEHYDE AS A PRODUCT OF THE PARTIAL COMBUSTION OF ORGANIC COMPOUNDS.*

By S. P. MULLIKEN, with J. W. BROWN and P. R. FRENCH.

IT has been shown elsewhere in the *American Chemical Journal*† by Mulliken and Scudder that formic aldehyde is apparently one of the most common products of the partial combustion of organic compounds by hot copper oxide, and that its appearance in minute traces as a result of such combustions ought never to be accepted as sufficient proof that the substance burned contains a methoxyl group. These conclusions were based entirely on qualitative experiments made incidentally in connection with a study of certain colour tests for methyl alcohol. The present investigation is quantitative in character. Its object is to furnish direct proof that the quantities of formic aldehyde which may be obtained from the oxidation of various typical and purified non-methoxylated compounds are, in general, greater than could arise from accidental impurities in the substances used.

Before proceeding to a description of these experiments, allusion should be made to the few scattering earlier investigations which have a more or less direct bearing on the matter under consideration. Legler (*Ann. Chem. Liebig*, ccxvii., 382; *Ber. d. Chem. Ges.*, xviii., 3343), claims to have found formic aldehyde in small quantities among the products of the phosphorescent combustion of ethyl ether in presence of metallic platinum. Pratesi (*Gazz. Chim. Ital.*, xiv., 221), obtained it from a decomposition of the vapours of boiling ethyl nitrate induced by a strip of incandescent platinum. Its formation was detected by Schützenberger (*Bull. Soc. Chim.*, xxxi., 482), when ethylene was heated with oxygen to 400°; and by Walkow and by Menschutkin (*Ber. d. Chem. Ges.*, xxxi., 3067), when a mixture of trimethylene and air was passed through a red-hot tube. Its occurrence to the extent of 0·5 per cent in wood smoke, which has lately been noted by Pasqualis (*Centrbl.*, 1897, II., 1012), may also be mentioned, although its appearance in this case is no doubt due merely to a secondary oxidation of the methyl alcohol, which is always formed when wood is subjected to destructive distillation.

In our experiments the oxidations were all made by means of the well-known, simple, and efficient apparatus devised by Loew (*Journ. Prakt. Chem.*, xxxiii., 324; *cf.* also Tollens in *Ber. d. Chem. Ges.*, xix., 2135), for the preparation of formic aldehyde from methyl alcohol. Loew early used this apparatus for the partial oxidation of several non-methoxylated substances. Ethyl ether, ethyl acetate, and ethylamine, all gave him acetaldehyde, while toluene yielded some benzaldehyde; but no substance other than methyl alcohol is mentioned as having given formic aldehyde, means for detecting small quantities of formic aldehyde in the presence of much acetic aldehyde being at that time unknown.

In Loew's method a stream of dry air, more or less fully saturated with a combustible vapour, is aspirated through a long tube of infusible glass containing a short coil of oxidised copper gauze, the latter being first brought nearly to redness by the temporary application of a gas flame. The copper oxide of the roll serving as an oxygen carrier, the roll continues to glow brightly, after the gas flame is withdrawn, as long as the combustible mixture is supplied. The liquefiable products of the reaction are condensed by passage through a series of well-cooled bottles containing water, which are interposed between the combustion tube and the suction-pump.

In our work the suction was supplied by a single Richards water aspirator run at nearly its full capacity. The combustion tube was 2 feet long and supported near its lower end by a clamp protected by asbestos. The copper roll, 2 inches in length, was made of fine-meshed gauze rolled loosely to fill the whole bore of the tube. The space within the tube above the coil was filled with fibrous asbestos, as a precaution against possible explosions, though none ever occurred.

The aspirated air, after being first dried by sulphuric acid, was passed rapidly through the liquid with whose vapours it was to be charged. The liquid was placed in a round-bottomed flask supported at such a height that a water-bath might be brought under it to raise the temperature, if desired. An exit-tube passing through the stopper of this flask conveyed the mixture of air and vapour into the combustion tube. The latter was drawn out and bent at its lower end so as to just dip beneath the surface of 50 c.c. of distilled water in the first of a series of four condensing bottles, each of which also contained water through which the gaseous combustion products were made to pass. Whenever a new vapour was to be burned, some preliminary experimenting was required to find the best temperature at which to maintain the evaporating liquid, and the proper rate at which to draw air through it. After the best conditions had been once ascertained, however, the combustion usually proceeded smoothly and with very little separation of carbon, the copper roll often maintaining its dull red glow for several hours without requiring any special attention from the experimenter. A few moments' application of a Bunsen burner flame was frequently quite sufficient to start the reaction, though there were cases in which the heating had to be continued for more than fifteen minutes. The ratio between air and vapour in the different experiments could not readily be kept constant, and bore no known relation to the theoretical quantities corresponding to any particular chemical equations. The composition of the mixtures and the rate of aspiration were simply such as experience showed were favourable to uninterrupted combustion. In experiments with the same substance the largest yields of aldehyde were often obtained when only half the roll was glowing.

Considerable time was spent in the search for a reliable analytical method for the determination of small quantities of formic aldehyde in presence of much acetic aldehyde. In the course of this search Mr. Brown studied nearly all the methods that have been proposed for the analysis of formic aldehyde solutions, and came to the conclusion that acetic aldehyde must always first be removed. The method of separation which was adopted was based on the fact, referred to in the article by Mulliken and Scudder, that acetic aldehyde may be completely boiled out from dilute aqueous solu

* Contributions from the Chemical Laboratory of the Massachusetts Institute of Technology. From the *American Chemical Journal*, xxv., No. 2.

† Volume xxiv., p. 446. Attention is here called to two slight corrections that should be made in the text of the article quoted. On page 451, line 21, insert the words, "*containing strong sulphuric acid*," between "second tube" and "held"; and on p. 452, line 18, read "*tertiary*," between "secondary" and "and butyl."

tions in such a way that practically all of the formic aldehyde will be held back by the water. To accomplish this result in the present instance, the liquid contents of all the condenser bottles were united, diluted to 500 c.c. with water, and placed in a round-bottomed litre flask connected with a long upright return-flow condenser. The upper end of the condenser was joined, by means of a descending glass tube, with a glass worm packed in ice and salt. The worm delivered into a flask surrounded by a freezing-mixture. The dilute aldehyde solution was gently boiled for two hours to drive over the acetic aldehyde. During the boiling, warm water at 45° to 50° was kept circulating through the condenser, the temperature being carefully controlled with the aid of a thermometer hung within the glass condenser jacket. It was found, by direct experiments, that the quantity of formic aldehyde vapour which passed over and was absorbed by water placed in the cooled receiver upon boiling a 1 per cent aqueous solution for two hours, as above described, was too small to be accurately determined, though its presence in the receiver could be shown qualitatively by the delicate gallic acid test. The removal of acetic aldehyde by the process was so complete that in the experiment on the oxidation of ethyl alcohol, in which 43 grms. of acetic aldehyde were produced, no trace of acetic aldehyde could be detected in the flask at the close of the two hours' boiling. A strong, unmistakeable formalin odour was, however, noticeable in each of the warm boiled solutions in which formic aldehyde was determined. These solutions also all gave very pronounced qualitative reactions for formic aldehyde, by the gallic acid, resorcin, and hexamethylenetetramine tetrabromide tests.

The determinations of formic aldehyde which follow were made by the colorimetric method of Trillat in essentially the form described by Wolff (*Ztschr. d. Nahr. u. Genuss.*, 1890, 89), though with certain added precautions.

The determinations of acetic aldehyde were obtained by the colorimetric method of Thresh (*Pharm. Journ.* [3], ix., 408), which was so far modified and improved as to give results which are trustworthy to within 2 per cent of their total value. Acetic aldehyde was tested for in all oxidation-products by adding solid sodic hydrate to a few centimetres of the mixed and diluted aqueous solutions until the liquid became almost syrupy, and then boiling for a minute or two. The least trace of acetic aldehyde then gave the characteristic aldehyde resin odour, and a deep yellow solution.

The compounds chosen for oxidation were Kahlbaum's best preparations, and were carefully rectified before use by distillation through a tall Le Bel-Henninger tower. Only the middle portion of a large fraction of correct and constant boiling point was used, unless it is otherwise stated in the record of the experiment. In the following brief statement of results the compounds studied follow one another in an order which corresponds to the quantity of formic aldehyde produced by their respective oxidations, the substance giving the largest yield closing the list. The experiments on acetone and ethyl alcohol were made by Mr. Brown, the remainder by Mr. French.

Summary of Experimental Results.

Acetone.—(Prepared from the pure bisulphide compound). 271 grms. gave 0·6055 grm. formic aldehyde, but no acetic aldehyde. Duration of oxidation, two and a half hours. Temperature of bath, 25° to 30°.—*Yield of formic aldehyde*, 0·22 *per cent.*

Ethyl Alcohol.—(Prepared from the purest absolute alcohol).—187 grms. gave gave 0·832 grm. formic aldehyde and 42·9 grms. acetic aldehyde. Duration of oxidation, three hours. Temperature of bath, 35° to 40°.—*Yield of formic aldehyde*, 0·44 *per cent.*

Pentane.—(Boiling point 35° to 37°). 119 grms. gave 1·05 grms. formic aldehyde, but no acetic aldehyde. No bath was employed.—*Yield of formic aldehyde*, 0·88 *per cent.*

Acetic Acid.—("99 to 100 per cent 'Kahlbaum's acid' free from homologues"). 232 grms. with the bath at 60° to 65° gave 1·95 grms. formic aldehyde, but no acetic aldehyde. The oxidation was very easily controlled and the copper roll no more disintegrated than in other experiments. Most of the unoxidised acid in the distillate was neutralised with calcium carbonate before determining the aldehyde.—*Yield of formic aldehyde*, 0·84 *per cent.*

Ethyl Oxide.—(Absolute ether distilled from sodium, boiling between 35° and 36°). 258 grms. gave 4·78 grms. formic aldehyde and 12·24 grms. acetaldehyde.—*Yield of formic aldehyde*, 1·86 *per cent.*

Amylene.—(Mainly trimethylethylene. Boiling point 37° to 40°). 100 grms. gave 2·01 grms. formic aldehyde, but no acetic aldehyde. No bath was used.—*Yield of formic aldehyde*, 2·01 *per cent.*

Normal Propyl Alcohol.—Boiling point 96° to 99°). 56 grms. with the bath at 45° to 50° gave 1·53 grms. formic aldehyde, but no acetaldehyde.—*Yield of formic aldehyde*, 2·72 *per cent.*

Trimethylcarbinol.—(Boiling-point 82° to 85°). 39 grms. gave 2·01 grms. formic aldehyde, but no acetaldehyde. Temperature of bath, 35° to 40°. The quantity of carbon dioxide formed in the experiment was unusually large.—*Yield of formic aldehyde*, 5·17 *per cent.*

An oxidation of 150 grms. of benzene, free from thiophene, with the bath at 45° to 50°, did not give formic aldehyde in determinable quantity. The oxidation of an equal weight of toluene gave very appreciable quantities of formic aldehyde, but quantitative determinations were not attempted, as it was found that benzoic aldehyde, which was also present, would prevent the successful employment of the Trillat method.

In comparing the yields of formic aldehyde obtained in these experiments, it must be remembered that the values recorded hold true for a single set of conditions only, and that these cannot always have been the most favourable ones possible. The important fact demonstrated is the marked tendency to the production of measurable quantities of formic aldehyde in the partial combustion of numerous carbon compounds belonging to very dissimilar types. So far as yet appears, this reaction is even of more frequent occurrence in such oxidations by air and copper oxide as have been described, than is the more familiar formation of oxalic acid in oxidations by nitric acid. Whether formic aldehyde, in small quantities, is also a frequent product of oxidations in the wet way, we have not attempted to determine. That it may be formed in many reactions of this class is, however, not in the least improbable.

ON THE METEORIC STONES WHICH FELL NEAR ZOMBA, BRITISH CENTRAL AFRICA, ON JANUARY 25TH, 1899. WITH NOTES ON THE CHEMICAL ANALYSIS OF SUCH BODIES.*

By L. FLETCHER, M.A., F.G.S.,
Keeper of Minerals in the British Museum.

(Continued from p. 6).

Part II.—The Characters of the Stones.

The Crust.

The crust is brownish-black to black in colour; it is mostly smooth, but in parts is scoriaceous or wrinkled; it shows occasional protuberances. The crust is dull, but a spot, 7 m.m. in diameter, on Stone No. 7 is lustrous; in the case of Stone No. 3 a patch of crust, 3 m.m. by 4 m.m. is transparent, and of a light green colour. On Stone No. 7 there is a linear ridge which can be traced

* From the *Mineralogical Magazine*, vol. xiii., No. 59, 1901.

round one of the edges of the stone for a distance of 70 m.m.; a fracture of the crust shows that the ridge is the prolongation of a black vein in the stone. The thickness of the crust averages 0·5 m.m., and reaches a maximum of 1 m.m.

Each of the stones Nos. 9 and 10 has one side different in aspect from the others; instead of being comparatively uniform in curvature, this side is covered with pit-like depressions.

The Fractured Surfaces.

The fractured surface of Stone No. 7 shows part of a broken troilite-nodule, 5 m.m. wide, of irregular form; an unbroken chondrule, 2 m.m. in diameter, projects above the general surface; in one part is a material of vitreous lustre, curved, nearly linear, and 2 m.m. long.

A freshly made fracture of Stone No. 3 varies in parts from white to whitish-grey in colour; one portion shows a dark grey oval patch, 12 m.m. by 7 m.m.; another was found to break through a beautifully regular bluish or bluish-grey chondrule, 2¼ m.m. in diameter.

Specific Gravity.

The specific gravity was determined for a fragment, weighing 13·8522 grms., of Stone No. 3; the fragment was free from crust, and exactly similar in aspect to a fragment of the same stone used for chemical analysis. The loss of weight in distilled water at 20°2° C. was 3·8973; the air was extracted from the pores by the air-pump. Duly corrected, the weight of 1 c.c. at 20°2° C. is 3·545 grms.

Microscopic Examination.

Thin sections prepared for the microscope, when examined with the unassisted eye, by reflected light, show small, very irregularly shaped, lustrous, metallic constituents (nickel-iron), and also still smaller dull opaque black particles (completely enclosed nickel-iron, troilite, or chromite), dispersed through a greyish-white stony material; one of the five sections shows part of a black vein. By ordinary transmitted light the stony material is seen with the aid of the microscope, to consist almost wholly of a nearly colourless crystalline groundmass, constituted of crystals which are chiefly small and rarely show any boundary due to the section of a natural face. Between crossed Nicols the groundmass (olivine, enstatite, and plagioclastic felspar), is seen as a bright small-grained mosaic (grey, yellow, red, blue, and green), interpersed with small and large crystals (the latter chiefly olivine); here and there, small quantities of a mineral nearly or quite free from cracks, and polarising in grey tints (probably plagioclastic felspar) fill up intervening irregular spaces, and mould the other crystallised material; the general aspect being very like that of sections of the meteorites of Lind County, Grossliebenthal, Girgenti, and Alfianello. Enclosed in the groundmass, and intimately connected therewith, are some chondrules, few in number, and almost all of them white. One of them is perfectly round, and has a well marked shell, the whole of the kernel and the shell extinguishing the light simultaneously (monosomatically), and being constituted apparently of short blocks, characters which are very common in olivine-chondrules: further, as is not unusual, particles of nickel-iron are closely grouped round the greater part of the outer boundary of the shell. A second chondrule is very similar, but no shell is evident, and the block-structure is less marked. A third chondrule, almost monosomatic, shows a triple shell. Other chondrules are polysomatic, being composed of several crystals having different optic orientations. In each of two slides is a section of a chondrule, which, looked at with the unassisted eye, is black by reflected light; with the microscope and crossed Nicols, it is seen to consist of a transparent substance polarising in grey tints (probably plagioclastic felspar) and enclosing opaque particles which are densely packed in the centre, and are almost absent near the circumference of the chondrule; a similar black chondrule is shown by a section of the Grossliebenthal meteorite Some patches of material seen in the sections are microcrystalline aggregates, and are possibly enstatite.

Chemical Examination.

As there is necessarily more or less speculation in the interpretation of the results observed during the chemical examination of a mechanical mixture of compounds having one or more chemical elements in common, the observations and calculations are conveniently kept quite distinct from each other, and recorded in separate sections. Both are given in detail, so that future investigators of meteoric stones may know the kind of difficulty which presents itself in such an inquiry, and may form an estimate of the weight to be assigned to the numerical results arrived at.

Section I.—Observations.

Weights obtained in the Course of the Chemical Analysis.

Magnetic Separation.

1. A freshly broken, easily frangible, crustless fragment of Stone No. 3, weighing 14·6 grms., was crushed in a steel mortar, and afterwards pulverised, in small portions at a time, in an agate mortar; it was impossible, owing to the presence of malleable grains of nickel-iron alloy, to reduce the material in this way to a fine powder of uniform composition. The alloy was next magnetically extracted by means of a seven-toothed iron comb, such as is used by grainers, but which had been magnetised; the powder being worked through in small quantities at a time. The residual powder was again pulverised in the agate mortar and the magnetic separation repeated. At the end of a series of operations the material had been divided into two parts; the one, attracted, weighing 2·0144 grms.; the other, unattracted, weighing 12·4208 grms.; the total quantity of material available for analysis being thus 14·4352 grms. The attracted material consisted of particles of different sizes; some of them were about a millimetre in diameter; much of the remainder consisted of smaller but still coarse grains, and another portion consisted of particles which were extremely minute, and thus readily oxidisable on exposure to air or moisture; the unattracted material was an impalpable powder of a bluish-grey colour and apparently quite free from iron-rust.

Attracted Material: Total Weight, 2·0144 Grms.

Treatment with Solution of Mercuric Ammonium Chloride.

2. 0·7421 grm. of the attracted material was transferred to a small flask, and treated with cold mercuric solution in an atmosphere of hydrogen as described in a previous paper (*Mineralogical Magazine*, 1894, vol. x., p. 293), the flask and contents being frequently shaken during the daytime; after the action had proceeded for some time, the liquid was quickly filtered, and the insoluble matter was washed with cold water which contained a little mercuric solution, and had been boiled to expel dissolved air. For each of the first two extractions 200 c.c. of the mercuric solution were used; for each of the next five, 100 c.c.; the first extraction was allowed to proceed for three hours; each of the next four, for twenty-four hours; the sixth, for ninety-six hours; and the seventh, for twenty-four hours.

Each of the extracts was acidified, heated to boiling, and precipitated by sulphuretted hydrogen, and the several filtrates were evaporated to dryness. The residue from the third extract showed by its colour that an appreciable amount of alloy had been extracted by the mercuric solution, and there was still an evident tinge of colour even in the residue from the seventh extract; the colouration was much smaller in the case of the fourth and fifth extracts than in that of the third, while those of the sixth and seventh, though evident, were only just appreciable; the last two were of about equal intensity, although the sixth extraction had occupied four days, and the seventh only one. There was by this time much admixed mercury and mercurous chloride, protecting the material to some extent from the action of the solvent; possibly, also, some of the

particles of the alloy were so large as to require a very prolonged action to produce solution; possibly some had been superficially oxidised, and were partially sheltered by the oxide from contact with the liquid; undissolved particles of alloy are very liable to be superficially oxidised when exposed to the air during the filtration. The extraction, although incomplete, was accordingly not further proceeded with at this stage.

The various precipitates produced by the sulphuretted hydrogen were ignited, and the mercury driven off; there remained a small brownish residue, which was soluble in warm hydrochloric acid, and gave a rich yellow solution; it was again precipitated by sulphuretted hydrogen, and the filtrate, which may contain a little iron carried down by the mercuric sulphide, was added to the main extracts. The brown precipitate weighed after ignition 0·0001 grm., and was found to be due to the presence of copper. The extracts having been collected together, the iron was oxidised, and at the same time the ammonium chloride decomposed, by evaporation with strong nitric acid; the residue was then treated with strong hydrochloric acid, and again evaporated to dryness. From the dilute solution the iron was separated from the nickel by a fourfold precipitation with sodium acetate; probably two precipitations would have sufficed, for it was afterwards found that the nickel separated by the third and fourth precipitations were scarcely large enough to be appreciable. After a final precipitation with ammonia and ignition, the precipitate weighed 0·4933 grm. Of this 0·4054 grm. was ignited in a current of hydrogen, and treated with hydrochloric acid; the insoluble SiO_2 weighed 0·0028, and was probably due to the action of the voluminous boiling liquid on the glass during the four precipitations of the iron. The dissolved iron was precipitated by ammonium sulphide, and the filtrate, which showed no trace of nickel (thus indicating the completeness of the separation from that metal), was evaporated to dryness; the ammoniacal salt was expelled by gentle ignition; from the residue then obtained, a small quantity of phosphorus (presumably due to oxidation of schreibersite, phosphide of iron, and nickel) was eventually separated by molybdic solution, and afterwards by magnesia mixture; the $Mg_2P_2O_7$ weighed only 0·0005.

The nickel and cobalt were twice precipitated by caustic potash and bromine water; as oxides they weighed 0·0606, as metal 0·0487. The cobalt was separated from the nickel by the nitrite method, and converted into potassium cobalt sulphate ($3K_2SO_4.2CoSO_4$); this weighed 0·0166.

3. The residue from the action of the mercuric solution was in two parts; one part, still adherent to the filter, weighed after ignition (and therefore partial oxidation), 0·0019 grm.; the other part, which had been washed from the filter, contained some bright metallic spangles (probably schreibersite, phosphide of iron, and nickel), mingled with much mercurous chloride, mercury, and coarse grains of silicate; further, much of the material was found to be still magnetic; after being heated in a current of hydrogen to a temperature just below visible red heat until no further volatilisation took place, it weighed 0·3366 grm. The residual powder, instead of consisting of light coloured silicates, as had been expected, was almost wholly of a dull black colour, but further contained the lustrous metallic spangles already referred to; and the whole was attracted by the compass-needle, showing that the coarse grains of silicate, obviously present, themselves contained magnetic matter. It was inferred that the powder consisted largely of magnetic oxide of iron; the residue was therefore heated to low redness in a current of hydrogen, again submitted to the action of the mercuric solution, transferred back to the boat, and again heated in hydrogen; as the residue was not much diminished and was still of a dull black colour, the operations were repeated, the temperature being raised to full red heat, but with a similar result. After a further extraction with mercuric solution, the residue was again heated in hydrogen to a full red heat, and weighed (0·2759 grm.) The part adherent to the filter weighed, after ignition, 0·0091 grm. The combined extracts yielded, after a double precipitation with sodium acetate, Fe_2O_3 0·0439, and Ni(Co) 0·0135.

4. As the total residue had only been reduced by the last operations from 0·3366 grm. to 0·2850 grm., and was not appreciably changed in aspect, it was decided to treat the residue with hydrochloric acid, and to analyse it in the same way as the unattracted material.

0·2757 grm. was treated on the water-bath with dilute HCl (s.g. 1·06); there was immediate effervescence, which lasted for ten minutes. From this it is inferred that particles of alloy had been protected from the mercuric solution by a coating of oxide or by enclosure in grains of olivinic silicate, probably in both ways. The silica set free by the acid was separated by means of sodic solution, and weighed (0·0447 grm.). The residue washed from the filter weighed 0·1280, and was white; the part adherent to the filter weighed, after ignition, 0·0129 grm.

From the acid solution the following weights were obtained:—

Fe_2O_3,SiO_2 0·0450 (yielding SiO_2 0·0013, presumably due to the action on the vessels.

Ni(Co)O 0·0088; yielding Ni(CO) 0·0072.

CaO 0·0036, probably almost entirely due to the action on the glass and porcelain during the precipitation of the iron and the separation of the nickel.

$Mg_2P_2O_7$ 0·1137.

Unattracted Material: Total Weight 12·4208 Grms.

Extractions with Water, Alcohol, and Ether.

5. 1·0017 grms. of the unattracted material was transferred to a platinum dish, and covered with 100 c.c. of distilled water; after being boiled the solution was allowed to cool, and then filtered without prolonged standing; the filtrate was opalescent. It was evaporated to dryness, 100 c.c. of water was again added, and the liquid was boiled. It was afterwards filtered, the filter being on this occasion being unwashed; the filtrate was now limpid, and yet contained all the soluble matter; the powder adherent to the dish and filter was doubtless finely divided silicate which had been in a state of suspension, and had caused the opalescence. The soluble residue yielded by the evaporation of the filtrate weighed 0·0026 grm., or 0·26 per cent.

Its solution was inactive to litmus and turmeric, and gave a rich yellow colour to the Bunsen flame. On spontaneous evaporation it began to deposit a precipitate as soon as it became concentrated, the liquid becoming quite milky in appearance when its volume had decreased to a cubic centimetre; after the evaporation was complete, the residue, examined with the microscope, was seen to consist mostly of small crystals optically isotropic, but of no distinct form; there were a few isolated groups of radiating birefringent plates, and also some isolated acicular crystals having straight extinction. The solution gave no precipitate with ammonia and ammonium chloride, even on boiling, but was found to contain calcium and a minute amount of magnesium. It contained sulphate in considerable quantity, but only an extremely minute trace of chloride; no phosphate could be detected. This is virtually the same result as was obtained in the examination of the Makariwa stone (*Mineralogical Magazine*, 1894, vol. x., p. 297); in that case it was inferred that the salts found in the extracting water were due to a partial oxidation of the protosulphide of iron (troilite) to sulphate, and to the subsequent action of the dissolved sulphate on the silicates, but it was uncertain whether the oxidation had taken place during the aqueous extraction itself or while the stone was lying buried in the ground. As the Zomba stone was quite fresh, it may be concluded that the oxidation of the troilite takes place during the boiling, and that the soluble salts may be accounted for without being regarded as original constituents of the meteoric stone.

The residue left after treatment with the distilled water

was digested with 50 c.c. of absolute alcohol for three days, and afterwards with 50 c.c. of ether for thirty minutes; in neither case was anything weighable extracted.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 20th, 1901.

Prof. EMERSON REYNOLDS, Sc.D., F.R.S., President, in the Chair.

(Concluded from p. 10).

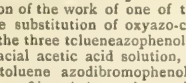
117. "*Action of Bromine on the Three Toluene Azophenols.*" By J. T. HEWITT and J. N. TERVET.

In continuation of the work of one of the authors and his pupils on the substitution of oxyazo-compounds, the bromination of the three tolueneazophenols has now been studied. In glacial acetic acid solution, sodium acetate being present, toluene azodibromophenols result in all these cases, the reactions being quite analogous to those observed with phenol itself. Metatolueneazophenol brominates smoothly only if the solution in acetic acid is well cooled whilst the bromine is added.

The following substances have been prepared:—*o-Tolueneazodibromophenol*, m. p. 121°; *ethyl ether*, m. p. 95°; *acetyl* derivative, m. p. 153°; *benzoyl* derivative, m. p. 169°; *m-tolueneazodibromophenol*, m. p. 129°; *ethyl ether*, m. p. 88°; *acetyl* derivative, m. p. 118°; *benzoyl* derivative, m. p. 141°; *p-tolueneazophenol*, m. p. 137°; *ethyl ether*, m. p. 95°; *acetyl* derivative, m. p. 148°; *benzoyl* derivative, 114°.

118. "*Reduction of αγ-Dibenzoylpropane and Dibenzoyldiphenylbutadiene.*" By F. R. JAPP, F.R.S., and A. C. MICHIE, B.Sc.

By the action of sodium on an ethereal solution of αγ-dibenzoylpropane, $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}C_6H_5$, floating on water, J. Wislicenus and Kuhn (*Annalen*, 1898, cccii., 221), obtained a "pale yellow oil," which they regard as the cyclic pinacone, 1:2-*diphenyl*-1:2-*dihydroxy*-cyclo*pentane*,—



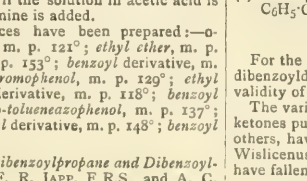
The present authors show that this oil is, in reality, a very complex mixture. The pinacone, which when pure forms colourless needles showing oblique extinction, and melting at 103—104·5°, is contained in it to the extent of about 50 per cent. From glacial acetic acid the pinacone is deposited in large, sparingly soluble crystals of the formula $C_{17}H_{18}O_2,C_2H_4O_2$, in which form it may be separated from the other substances present. A quantitative yield of it may be obtained by the reduction of dibenzoylpropane in hot aqueous alcoholic solution with aluminium amalgam. Oxidised with chromium trioxide, it regenerates dibenzoylpropane. In addition to the pinacone, the "pale yellow oil" contains, along with other substances, a small quantity of *αε-diphenyl-αε-dihydroxypentane*,—

$$C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}C_6H_5,$$

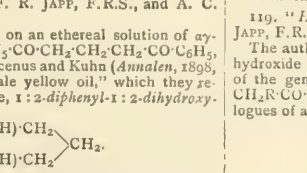
lustrous, slender, six-sided prisms showing straight extinction, and melting at 84—88° to a turbid liquid which clears at 92°. A better although still unsatisfactory yield of the latter substance is obtained by reducing dibenzoylpropane in boiling alcoholic solution with sodium.

By reducing the "pale yellow oil" with hydriodic acid, Wislicenus and Kuhn prepared a hydrocarbon melting at 108° to which they assign the constitution of a 1:2-*diphenylcyclopentane*. The authors find that this supposed 1:2-diphenyl*cyclo*pentane is a highly polymerised substance which does not boil even at 340° under a pressure of 12 m.m., whereas the known 1:2-diphenyl*cyclo*pentane (m. p. 47°) obtained from anhydracetonebenzil (Japp and Burton, *Trans.*, 1887, li., 423; Japp and Lander, *Trans.*, 1897, lxxi., 128 and 131), the existence of which has been overlooked by Wislicenus and Kuhn, boils at 189° under a pressure of 12 m.m. The authors give a further proof of the constitution of the latter 1:2-diphenyl*cyclo*pentane by oxidising it to αγ-dibenzoylpropane.

J. Wislicenus and Lehmann (*Annalen*, 1898, cccii., 214), by reducing dibenzoyldiphenylbutadiene with hydriodic acid, obtain, along with other products, a substance melting at 92—94°, to which they assign the formula $C_{20}H_{14}O$. The authors find that this compound has in reality the formula $C_{22}H_{16}O$, and is 2:3:5-*triphenylfurfuran* (Japp and Klingemann, *Trans.*, 1890, lvii., 663), and that *acetophenone* is simultaneously formed, the reaction taking place as follows:—



αβ-Dibenzoylphenylethylene.

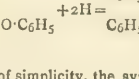


For the sake of simplicity, the symmetrical formula for dibenzoyldiphenylbutadiene has been employed; but the validity of the explanation is quite independent of this.

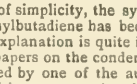
The various papers on the condensations of benzil with ketones published by one of the authors, conjointly with others, have, with one exception, been overlooked by J. Wislicenus and his pupils, and the errors into which they have fallen are in part attributable to this cause.

119. "*Homologues of Anhydracetonebenzil.*" By F. R. JAPP, F.R.S., and A. N. MELDRUM, B.Sc.

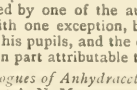
The authors find that under the influence of potassium hydroxide benzil condenses with homologues of acetone of the general formulæ $CH_2R{\cdot}CO{\cdot}CH_3$, $CHR_2{\cdot}CO{\cdot}CH_3$, $CH_2R{\cdot}CO{\cdot}CH_2R$, and $CHR_2{\cdot}CO{\cdot}CH_2R$, to form homologues of anhydracetonebenzil (*diphenyl*cyclo*pentenolone*),



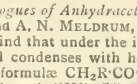
In naming these compounds the CH group in the pentacarbon ring is distinguished as the α- and the CH_2 group as the β-position. Thus benzil and methyl ethyl ketone yield *α-methylanhydracetonebenzil*,—



(large, flat, lozenge-shaped crystals, melting at 118°), and *β-methylanhydracetonebenzil*,—



(prisms, melting at 180°)—the latter already prepared by Japp and Burton (*Trans.*, 1887, li., 431)—whilst at the same time an open-chain compound, *desylene-methyl ethyl ketone*,—



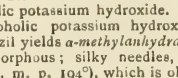
(m. p. 157°), is formed. The latter substance is more readily obtained by boiling β-methylanhydracetonebenzil with glacial acetic acid, and, on the other hand, is re converted into the β-compound by heating at 300—320°.

The authors show that the sparingly soluble monalkyl homologues of anhydracetonebenzil prepared by Japp and

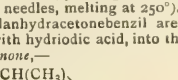
Burton by heating a mixture of benzil and homologues of acetone with aqueous potassium hydroxide, belong to the β-series, and that readily soluble α-isomerides, overlooked by these authors, are formed in small quantity at the same time. By using cold alcoholic potassium hydroxide as a condensing agent, the α-compounds may be obtained in larger quantity. All the α-compounds are distinguished by forming benzylidene derivatives when treated with benzaldehyde and alcoholic potassium hydroxide.

With benzil and alcoholic potassium hydroxide, α-methylanhydracetonebenzil yields *α-methylanhydracetonedibenzil*, $C_{32}H_{26}O_4$ (dimorphous; silky needles, m. p. 185°; and warty crystals, m. p. 194°), which is obtained in the form of a complex potassium salt, $C_{32}H_{25}O_4K,C_{32}H_{26}O_4,4C_2H_5{\cdot}OH$. The sodium salt may be obtained directly from benzil and methyl ethyl ketone by condensation with alcoholic sodium ethoxide. α-Methylanhydracetonedibenzil is ethylated by boiling it with alcohol and sulphuric acid, yielding the compound $C_{32}H_{25}(OC_2H_5)O_3$ (short needles, melting at 250°).

Both α- and β-methylanhydracetonebenzil are transformed, by brief boiling with hydriodic acid, into the same *methyldiphenylcyclopentenone*,—



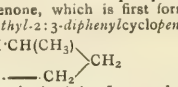
(faint yellow, oblique, flat prisms or plates, m. p. 77—78°), which yields a *phenylhydrazone*, $C_{24}H_{22}N_2$, melting at 145—152°. By boiling α-methylanhydracetonebenzil for five hours with hydriodic acid and red phosphorus, the methyldiphenylcyclopentenone, which is first formed, is in its turn reduced to *1-methyl-2:3-diphenylcyclopentane*,—



(m. p. 62—63°), already obtained by Japp and Murray (*Trans.*, 1897, lxxi., 153), by the reduction of α-anhydrobenzillævulic acid, the carboxyl group being eliminated in the latter case.

By boiling with slightly diluted sulphuric acid, or with glacial acetic acid, α-methylanhydracetonebenzil yields a dehydration product, $C_{36}H_{28}O_2$ (m. p. 230°, with evolution of gas. β-Methylanhydracetonebenzil, when heated with formic acid, gives the same product.

In addition to the foregoing, the following compounds have been prepared:—*Benzylidene-α-methylanhydracetonebenzil*, m. p. 225°; *α-desylene-ethyl ethyl ketone*,—



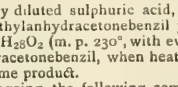
m. p. 128°, converted, on heating, into *αβ*-dimethylanhydracetonebenzil, m. p. 150°; *ββ-dimethylanhydracetonebenzil*, m. p. 181°; *α-ethylanhydracetonebenzil*, m. p. 114°, and its *benzylidene* derivative, m. p. 178°; *αββ-trimethylanhydracetonebenzil*, m. p. 131°; *α-propylanhydracetonebenzil*, m. p. 89°; and its *benzylidene* derivative, m. p. 166°; *β-propylanhydracetonebenzil*, m. p. 152°; *αβ-diethylanhydracetonebenzil*, m. p. 113—114°; *α-amylanhydracetonebenzil*, m. p. 57°; and its *benzylidene* derivative, m. p. 156°.

All β-monalkylanhydracetonebenzils corresponding with these α-compounds, but not included in the foregoing list, have been already described by Japp and Burton (*loc. cit.*).

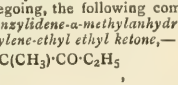
The oxidation products of the various methylanhydracetonebenzils are at present under investigation.

120. "*Formation of Carbazoles.*" (A Preliminary Note). By F. R. JAPP, F.R.S., and W. MAITLAND, B.Sc.

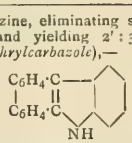
The fact that β-phenanthrol (*phenanthrone*),—



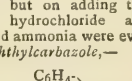
interacts, apparently in the keto-form,—



with phenylhydrazine, eliminating simultaneously water and ammonia, and yielding 2′:3′-diphenyleneindole (*phenyl β-phenanthrylcarbazole*),—



as in E. Fischer's synthesis of indoles (compare Japp and Findlay, *Trans.*, 1897, lxxi., 1117), led the authors to try whether β-naphthol, which β-phenanthrol in many respects resembles, would behave in an analogous manner. On heating β-naphthol with excess of phenylhydrazine there was no reaction, but on adding to the mixture some phenylhydrazine hydrochloride and continuing the heating, water, and ammonia were evolved, and a fair yield of a *phenyl-β-naphthylcarbazole*,—

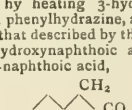


(needles melting at 134—135°), was obtained. The reaction does not take place when β-naphthol is heated with phenylhydrazine hydrochloride alone.

The following derivatives of this carbazole were prepared and analysed:—*Nitroso*-derivative, yellow flat needles, m. p. 144—145° (with decomposition); *acetyl* derivative, small pearly laminæ, m. p. 149°; *benzoyl* derivative, slender needles, m. p. 189·5°.

Two phenyl-β-naphthylcarbazoles—the number predicted by theory—are already known; one melting at 330°, isolated by Graebe and Knecht from coal-tar, and afterwards synthesised by them by passing the vapour of phenyl-β-naphthylamine through a red-hot tube (*Annalen*, 1880, ccii., 1); and a second obtained by Schöpff (*Ber.*, 1896, xxix., 269), by elimination of carbon dioxide from phenyl-β-naphthylcarbazolecarboxylic acid, and asserted by him to melt at 120°. The melting-points of the derivatives are given by Schöpff as follows:—*Nitroso* derivative, 132°; *acetyl* derivative, 142°; *benzoyl* derivative, 170°. With the exception, however, of these very considerable differences in the melting-points, the descriptions given by Schöpff of his compounds would apply to those prepared by the authors; moreover, various colour reactions which he mentions are the same in both cases. The authors, therefore, prepared Schöpff's phenyl-β-naphthylcarbazole by his method, and found that it melted at 134—135° (instead of at 120°, as stated by him), and was absolutely indistinguishable from their compound. As the yield by Schöpff's method is very poor, they did not trouble to prepare the derivatives over again from substances obtained in this way; but they have no doubt that similar errors in the determination of the melting-points have been committed by the German investigator in the case of these also.

Schöpff obtained his phenyl-β-naphthylcarbazole carboxylic acid by heating 3-hydroxy-β-napthoic acid (m. p. 216°) with phenylhydrazine, a reaction which would correspond with that described by the authors, except that this so-called hydroxynaphthoic acid is the keto-form dihydro-2-keto-3-naphthoic acid,



and that the addition of phenylhydrazine hydrochloride is unnecessary.

α-Naphthol, when heated with the mixture of phenylhydrazine and its hydrochloride, yielded *phenyl-α-naphthylcarbazole* (m. p. 225·5°), already obtained by Kym (*Ber.*, 1890, xxiii., 2465), by desulphurising thiophenyl-α-naphthylamine with finely divided copper. The present reaction does not take place so readily as with β-naphthol, and the yield is small.

The authors are engaged in extending this reaction to other phenols, and to other arylhydrazines in presence of their hydrochlorides.

121. "*Metal-ammonia Compounds in Aqueous Solution.* Part III. *Solutions of Salts of the Alkaline Earth Metals.*" By H. M. Dawson and J. McCrae.

The distinction of ammonia between solutions of salts of the alkaline earth metals and chloroform has been determined at 20°, and the results obtained indicate that the calcium ions form complex ammonia ions to a slight extent in solution, whilst the strontium ion possesses the power of fixing ammonia in a less degree, and the barium ion has the lowest power.

122. "*Metal-ammonia Compounds in Aqueous Solution.* Part IV. *The Influence of Temperature on the Dissociation of Cupri-ammonia Sulphate.*" By H. M. Dawson and J. McCrae.

The distribution of ammonia between water and chloroform, and between aqueous copper sulphate and chloroform has been determined at 10° and 30°. The results indicate that the copper sulphate fixes more ammonia at the lower than at the higher temperature; but no exact quantitative statement can be made as to the influence of temperature on the dissociation of the compound $Cu_4NH_3{\cdot}SO_4$, since within the limits of temperature at which the experiments were made this influence is very small.

The same relationship between ammonia concentration and distribution coefficient has been found at 10° and 30° as that previously observed at 20° (*Trans.*, 1901, lxxix., 496).

123. "*On the Combined Action of Diastase and Yeast on Starch-granules.*" By G. H. Morris, Ph.D.

When yeast is allowed to act on a solution of starch-conversion products in the presence of active diastase, the quantity of matter fermented is greatly in excess of that which can be fermented by the yeast alone; and when active diastase and yeast are allowed to act conjointly on the so-called stable-dextrin, which under ordinary conditions is neither degradable by diastase nor fermentable by yeast, it is entirely fermented.

It is now shown that a similar action takes place when certain ungelatinised starch-granules are submitted to the joint action of malt extract and yeast, the quantity of starch decomposed by the joint action being about three times that dissolved by malt-extract alone. The increased action in the presence of yeast is not due to the removal of the soluble product, maltose, from the field of action, and the consequent greater activity of the diastase. No increased diastatic action takes place in the presence of yeast if the fermentative power of the latter is checked by chloroform, neither does any increase of action take place when the malt-extract is submitted to fermentation, and the yeast-cells removed, before the addition of the starch-granules.

Precipitated diastase behaves in the same way as cold water malt-extract, but to a lesser extent.

The combined action of diastase and yeast only occurs with those starches which are attacked in the ungelatinised form by diastase, such as barley or malt starch. The granules of potato starch are not acted on by diastase even in the presence of yeast.

124. "*A Calibrating Mercury Pipette.*" By C. A. Bell, M.B.

The little device figured in the diagram will be found very useful in calibrations of all kinds. It is easily constructed on any scale; the volume of mercury delivered by it is for all practical purposes constant, and the time saved by its use is considerable.

The mercury reservoir, A, is made from a piece of soft German or soft Jena tubing, of moderate wall thickness, and free from internal flaws. At the lower end it is drawn out to a narrow tube terminating in an orifice about 0·4 m.m. in diameter. The edge of this orifice may be slightly fused, but not so as to invert it. At its upper end, A is drawn out to a very fine capillary tube, which should be of such diameter at its narrowest section that a pressure of *at least* 15 c.m. of mercury is required to drive the metal through it. A short tube of such narrow bore is not easily prepared in an ordinary blowpipe or Bunsen flame; the final drawing may, however, be easily effected in the outer mantle of a candle-flame, as in preparing a Lippmann's capillary electrometer. The little tube so formed should be cut at such a point that the diameter of the portion left on A (from 1 to 1·5 c.m. in length), diminishes continuously from A to the end. A constantly increasing pressure is then required to drive mercury nearer and nearer to the orifice.

The reservoir A thus prepared is cemented, as shown, air-tight into a somewhat wider tube, B, which is drawn out at its upper end so that an india-rubber tube may be attached to it. The cement used may be sealing-wax, but if B is just wide enough to receive A, a much neater joint may be made with fused silver chloride. A little of the chloride is melted in a porcelain crucible, and the well heated end of B dipped into it repeatedly until a sufficient quantity of the chloride has been collected. That which adheres to the inner surface of B is removed with a penknife; the previously warmed end of A is then passed into B, and the two tubes heated together high above a Bunsen flame, to avoid reduction of the silver, until the chloride melts. When prepared in this way, the pipette may be heated and dried by a current of air, if necessary, without disconnecting A and B.

To use the pipette, an india-rubber tube of some length is slipped over the narrow end of B, and secured air-tight by a few turns of soft copper wire, the ends of the wire being left loose. The point of the pipette is then plunged well below the surface of mercury contained in a bottle or basin, and suction applied until the metal rises to within a couple of millimetres of the capillary orifice. If the capillary tube has been properly formed, it can, without the slightest difficulty, be brought to any desired level which may be marked on the outside of B; but generally it is sufficient to bring it within a short distance of the orifice. A rather coarse capillary measured by a microscope micrometer was found to have, at the orifice, a diameter of 0·008 c.m. The capacity of a tube of this diameter is only 0·00005 c.c. per centimetre of length, so that a variation in the level of a millimetre either way is of small importance.

The filling having been accomplished, the rubber tube

is pinched; the pipette may then be lifted and carried about without the loss of a particle of mercury, so long as it is held in a nearly vertical position. Inclining it, however, by increasing the effective pressure on the capillary, may cause mercury to pass from A to B. This is much less likely to happen when in the process of filling the mercury has not been drawn right up to the orifice; the pressure may then increase or diminish considerably without causing the escape of mercury from either end of A.

In discharging the pipette, the pressure of the fingers on the rubber tube having been released, the mercury is allowed to trickle gently down the side of the tube or vessel to be calibrated. Usually a short thread of metal remains in the lower prolongation of A; this is best removed by pinching the rubber tube near its open end with the fingers of the hand holding the pipette, and compressing it about its centre with the other hand. It is not advisable to blow into B, as in the course of a calibration moisture from the breath may find its way into A, causing the formation of air bubbles within it.

As air bubbles never form in A when the mercury entering it is dry and free from surface impurities, any sensible variation in the volume delivered at constant temperature can be due only to variations in the point at which disruption occurs in the mercury when the pipette is raised. These, however, are exceedingly small. In a series of tests with a pipette holding about 17 grms. of mercury, and having an outflow orifice of 0·05 c.m. in diameter, the weight of mercury delivered was constant within 0·0005 grm., or in volume 0·00004 c.c. By making the outflow orifice very small, still greater constancy can be secured; but the time occupied in charging and emptying is then greatly increased. In conducting a test of this kind, of course the temperature of the mercury must be carefully observed. Mercury contained in a bottle or jar can never be assumed to be at room temperature, and when poured into a basin its temperature may alter rapidly from a variety of causes.

Sometimes a small globule of metal sticks very persistently in the lower constricted part of A. Such a globule can usually be rinsed out by sucking back a little of the metal already delivered, especially if the part of the tube containing it has been previously warmed.

The advantages of this pipette over Bunsen's well-known calibrating device are obvious. The quantity of mercury required for any calibration is a minimum; the metal need never be touched by the fingers; and as surface impurities are excluded by the pipette, which acts as a filter, the mercury delivered by it is always bright and clean, and lies in perfect contact with the wall of the receiving vessel.

125. "*α-Amido-β-methylhydrindene.*" By F. S. Kipping and G. Clarke.

The authors have prepared α-amido-β-methylhydrindene,—

$$C_6H_4\langle\begin{matrix}CH_2\cdot CHMe\\ CH(NH_2)\end{matrix}\rangle,$$

in order to study the salts obtained by combining it with various optically active acids, and thus perhaps to elucidate the curious behaviour of its lower homologue hydrindamine (Kipping, *Trans.*, 1900, lxxvii., 861; and Kipping and Hall, *Trans.*, 1901, lxxix, 442).

β-Methylhydrindone,—

$$C_6H_4\langle\begin{matrix}CH_2\\ CO\end{matrix}\rangle CH\cdot Me,$$

is easily obtained by the action of aluminium chloride on α-methylhydrocinnamic chloride, ring formation taking place with the elimination of hydrogen chloride (compare Kipping, *Trans.*, 1894, lxv., 680; Kipping and Hill, *Trans.*, 1899, lxxv., 144; and Kipping and Hunter, *Trans.*, 1901, lxxix., 604).

This method gives much better results than the treatment of the acid with concentrated sulphuric acid (von Miller and Rhode, *Ber.*, 1890, xxiii., 1888), the yield being from 70 to 80 per cent of the theoretical.

β-Methyl-α-hydrindoxime crystallises in well-defined octahedra, melting at about 103°. The base, of which the formula is given above, is obtained by reducing the oxime with sodium amalgam in dilute acetic acid solution. It resembles hydrindamine in general properties.

Since α-amido-β-methylhydrindene contains two asymmetric carbon groups, it should consist of four optically different forms, and when combined with optically inactive acids it might be expected to give rise to two series of salts.

As a matter of fact, on fractionally crystallising the *hydrochloride* of the original base from water, it is resolved into a sparingly soluble salt, which forms long, silky needles, decomposing at about 252°, and a readily soluble salt which is obtained in small, ill-defined nodular masses decomposing at about 225°.

The two hydrochlorides are probably the salts of the two externally compensated

$$\left(\begin{matrix}+ & -\\ + & -\end{matrix}\text{ and }\begin{matrix}+ & -\\ - & +\end{matrix}\right)$$

bases, but the more readily soluble one may not be quite free from its isomeride. The sparingly soluble salt gives a *platinichloride*, $(C_{10}H_{13}N)_2,H_2PtCl_6+2H_2O$, which crystallises from water in lustrous, yellow plates, decomposing at about 192°, whilst the readily soluble isomeride gives a *platinichloride*. $(C_{10}H_{13}N)_2,H_2PtCl_6$, which is anhydrous, and decomposes at about 202°.

The *benzoyl* derivative prepared from the sparingly soluble hydrochloride crystallises in silky needles, melting at 169°, whereas the corresponding compound, obtained from the readily soluble hydrochloride, melts at about 138°.

The *sulphate* of the original base crystallises in large transparent prisms, and does not seem to be resolved into different products when fractionally crystallised from water.

The investigation of these bases is being continued.

126. "*Stereoisomeric α- and α'-Sulphonic Derivatives of Camphor.*" By H. E. Armstrong and T. M. Lowry.

The authors have further examined Reychler's camphorsulphonic acid, prepared by sulphonating camphor by means of a mixture of sulphuric acid and acetic anhydride; they have also prepared corresponding acids from chloro- and bromo-camphor, which are reducible to Reychler's acid. They confirm Reychler's observation that two camphorsulphonamides are formed by the action of ammonia on the sulphochloride, and show that this is not due to any want of homogeneity in the latter, but to the occurrence of isomeric change during the interaction.

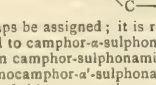
Reychler's camphorsulphonic acid is probably an α-acid, the sulpho-group occupying the same position as the bromine atom in α-bromocamphor. When the sulphochloride or sulphobromide is acted on with dilute ammonia the action proceeds normally, only the α-sulphonamide, m. p. 223°, being produced; the isomeric α'-sulphonamide, m. p. 132°, is formed when strong ammonia is used, and the action is allowed to proceed violently; it is a labile substance, and is readily converted into the stable α-sulphonamide by the action of bromine or of mineral acids.

Camphor-α-sulphobromide, m. p. 93°, $[\alpha]_D$ +26°. *Camphor-α-sulpho-p-bromoanilide*, m. p. 165°, $[\alpha]_D$ +56°. *Camphorsulphopiperidide*, m. p. 140°, $[\alpha]_D$ +32·2°, is the chief product of the action of piperidine on the sulphochloride, but a more soluble *piperidide*, m. p. 55°, $[\alpha]_D$ +33·6°, is also produced.

α-Bromocamphor-α'-sulphonic acid is readily isolated in the form of the *calcium* salt, $(C_{10}H_{15}SO_4)_2Ca+6H_2O$; this crystallises from hot water in pearly scales. The *sulphochloride*, m. p. 65°, $[\alpha]_D$ +104°, yields a single *sulphonamide*, m. p. 156, $[\alpha]_D$ +106°, which is reduced by zinc dust and acetic acid to camphor-α'-sulphonamide. The *sulphoanilide*, m. p. 106°, $[\alpha]_D$ +177° is reduced to camphor-α-sulphoanilide. The *sulphopiperidide*, m. p. 123°, $[\alpha]_D$ +111° is reduced to the camphorsulphopiperidide, melting at 140°.

α-Chlorocamphor-α'-sulphochloride has m. p. 60°, $[\alpha]_D$ +81°. The *sulphonamide*, m. p. 141° $[\alpha]_D$ +83° is reduced to camphor-α-sulphonamide.

When α-bromocamphor-α'-sulphonamide is boiled with acetic anhydride it is converted into an *anhydride*, $C_{10}H_{11}BrSO_2N$, m. p. 186°, $[\alpha]_D$ +98°, to which the formula—



may perpaps be assigned; it is reduced by zinc dust and acetic acid to camphor-α-sulphonamide. By the action of bromine on camphor-sulphonamide or of bromhydric acid on α-bromocamphor-α'-sulphonamide, the *stereoisomeric anhydride* of α'-bromocamphor-α-sulphonamide, m. p. 166°, $[\alpha]_D$ +41°, is also produced. By the further action of bromine these are converted into the *anhydride*, $C_{10}H_{13}Br_2SO_2N$, of a *dibromocamphorsulphonamide*, m. p. 195°, $[\alpha]_D$ −7°, which on reduction yields camphor-α-sulphonamide.

The *anhydride* of *α-chlorocamphor-α'-sulphonamide*, m. p. 167°, $[\alpha]_D$ +60°, yields camphor-α-sulphonamide on reduction. An *anhydride*, $C_{10}H_{13}Cl_2SO_2N$, of a *dichlorocamphorsulphonamide* may be prepared by the action of chlorine on camphorsulphonamide, chlorocamphorsulphonamide, or its anhydride; m. p. 172°, $[\alpha]_D$ +4°, on reduction this yields camphor-α-sulphonamide.

127. "*Displacement of Alkyls from Phenols by Nitration. I. Thymol.*" By A. T. LARTER.

Maldotti, in a recent note (*Gazetta*, 1900, xxx., II., 365), states that trinitrothymol is formed on nitrating dinitrothymol; he was unable to analyse the product, and bases his statement solely on molecular weight determinations made by the cryoscopic method. This conclusion is in opposition to the result arrived at by Armstrong and Rennie (CHEMICAL NEWS, 1883, xlvii., 115), who found that the so-called trinitrothymol was in reality trinitrometacresol.

The author has repeated the experiments at Dr. Armstrong's request, and his results confirm the conclusion arrived at by Armstrong and Rennie.

The melting-point of the product from thymol is the same as that of trinitrometacresol, and is unaffected when the substance is mixed with the trinitro-compound prepared from metacresol. On methylation, the product affords an ether identical with that prepared from trinitrometacresol, the two substances melting at 91°, whether singly or in admixture, and giving the same trinitrometatoluidine (m. p. 136°) when subjected to the action of ammonia.

When dinitrothymol ethyl ether is subjected to nitration, it is converted into trinitrometacresol ethyl ether—an observation of importance as proving that the displacement of the alkyl does not involve the formation at an intermediate stage of a keto-compound.

128. "*Taka-diastase and Reversed Ferment Action.*" By A. C. HILL.

The hydrolysis of dilute starch solutions by taka-diastase ends in an almost complete transformation to glucose, as shown by the combined polarimetric and copper reduction methods of estimation; no dextrin which resists further hydrolysis is formed, and there is sufficient maltase in commercial taka-diastase to convert all the maltose to glucose.

A solution containing 35 per cent of glucose and 6 per cent of maltose hydrate, that is, 41 per cent of total sugar, on treatment by taka-diastase containing maltase, was further hydrolysed until the measurements indicated nearly 39 per cent of glucose, and about 2 per cent of maltose hydrate. A 60 per cent solution of glucose, however, similarly treated, showed a reversed ferment action until its optical and reducing properties corresponded with those of a solution containing 58 per cent of glucose, and 2 per cent of maltose hydrate. On diluting the solution without boiling, hydrolysis again took place. The difference in equilibrium point in this case from that found by the author when acting on concentrated glucose solutions with yeast extract (*Trans.*, 1898, lxxiii., 634) (in the latter case the measurements at equilibrium corresponded to a mixture of 34 per cent of glucose, and 6 per cent of maltose hydrate), is probably to be explained by the presence in the yeast extract of enzymes other than maltase and diastase, whereby other polysaccharides are formed either from glucose or maltose, such ferment actions being quite distinct from a possible formation of higher polysaccharides from maltose, which may occur also in the case of taka-diastase.

CORRESPONDENCE.

THE DIRECT ESTIMATION OF CARBON IN METALS.

To the Editor of the Chemical News.

SIR,—The accurate estimation of carbon in metals by direct combustion in a stream of air or oxygen depends chiefly on the available temperature and the kind of reagent the powdered sample is mixed with. With regard to temperature one has frequently not much choice; being given a particular form of combustion furnace and a limited supply of gas. With regard to reagents we have from time to time had the following suggested :—

Powdered pumice, potass. chloride, potass. chromate, acid potass. sulphate, metallic lead, lead chromate, lead peroxide, litharge, red-lead, metallic copper, copper oxide, phosphor-copper, stannic oxide, zinc oxide, manganic oxide, and alumina.

For a particular kind of alloy each of the above may be effective, just as burning with no reagent at all may be (see CHEMICAL NEWS, lxxxi., 91); but with the most refractory alloy the steel-maker uses—ferrochromium—many of the above are no use whatever, except when employed at such temperatures as are generally not provided for in the laboratory.

The cheapest and perhaps most effective of the above reagents are the oxides of lead. The monoxide really ought not to be used if kept in the powdered state, because it readily absorbs both water and carbon dioxide from the atmosphere. Both the peroxide and red-lead serve very well if they can be obtained of such quality that no serious increase in weight of the KHO bulb takes place when they are ignited alone.

But unfortunately it is not easy to obtain either the peroxide or red-lead to meet this requirement, and one is therefore obliged to estimate the "blank" in as many samples as can be had and choose the best.

This is the game I have played for more than a year with red-lead, and I am now wiser by this much only :—The "blank" is generally greater in those samples which have the lighter colour, and is probably due to the carbon dioxide absorbed by that proportion of the PbO not needed to form Pb_3O_4.

The "blank" on 10 grms. of the worser kinds of red-lead may be as much as a decigrm. Ten grms. of the best kind yet met with gave a "blank" of nearly a centigrm., and this was picked up casually during a visit to some paint works.*

Red-lead yielding a constant blank of 1 centigrm. on 10 grms. is as good in respect to impurity as many other reagents. As 6 grms. Pb_3O_4 is an ample allowance for 1 grm. of the powdered alloy, it involves a correction amounting to only 0·16 per cent carbon. A correction of this magnitude is not serious, except perhaps in the somewhat rare cases where nearly pure chromium metal, said to be free from carbon, is being examined.

In order to avoid the "blank" altogether any of the

* The firm in question have been persuaded to keep for retail sale the large cask from which the sample was taken. Their address may be had on application.

oxides of lead may be fused in the boat, and then, after cooling, the finely powdered alloy spread evenly over the surface. The reaction is naturally much less active than when the mixture is made with the dry powder, and consequently the combustion needs a longer time, and the results are somewhat uncertain.

When economy is no consideration, the sesquioxide of bismuth, made by fusing the basic nitrate in the muffle, grinding, and sieving, gives quite as good results in as satisfactory a manner as the oxides of lead do, and the fact that it can be prepared in this manner so as to yield no blank makes it a very serviceable reagent for low carbon alloys.—I am, &c.,

HARRY BREARLEY.

Totley, near Sheffield.
July 4, 1901.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxii., No. 24, June 17, 1901.

Researches on Chemical Equilibrium. Formation of Insoluble Phosphates by Double Decomposition. Dibasic Sodium Phosphate and Silver Nitrate.—M. Berthelot.—The total precipitation of silver in the form of phosphate during the reaction of disodium phosphate on silver nitrate takes place in the cold, only when the two salts react in molecular proportion, the phosphoric acid existing in solution under the form of the mono- and di-basic salts. The total precipitation of phosphoric acid under the form of silver phosphate only takes place when three molecules of silver nitrate to one molecule of disodic phosphate are used with the final addition of soda in sufficient proportion to neutralise the acid excess; phenylphthalein being used as an indicator. In all cases the initial mixture gives place to phenomena of equilibrium between the two acids, from which, except in the first case, the formation of a certain quantity of soluble silver phosphate results. Finally, the precipitates formed in presence of an excess of phosphate contain, in addition to the predominant di-silver phosphate, a certain quantity of di-silver and silver-sodium phosphates; that is to say, the double salts, characteristic of the final state of the system, as is the case in the great majority of phenomena of chemical equilibrium.

New Syntheses effected by means of Molecules containing the Methylene Group Associated with one or two Negative Radicles. Action of Epichlorhydrine and Epibromhydrine on Sodium Benzoyl Acetic Ethers.—A. Haller.—The author's experiments show that the molecules which contain the ethylene oxide group, such as epichlorhydrine or epibromhydrine, are added directly and in the cold, to the sodium derivatives of the bodies containing $CH_2\diagup\!\!\diagdown\begin{matrix}R\\R'\end{matrix}$ (R and R' being the negative radicals), and probably also to the bodies containing the complex radicle—CHNaCO—or the tautomeric complex radicle—CH=CONa. In the case where the β-ketonic ethers are used, the halogen keto-oxyacids are the first things obtained; these when liberated from their soda salts are transformed into halogen keto-actones of the form $\begin{matrix}R.CO.CH—CO\\|\qquad\quad>O\\CH_2.CH—CH_2Cl\end{matrix}$. These halogen keto-actones are susceptible under the influence of alkalis of giving rise to ketone-glycols, of which up to the present time scarcely any representatives are known. On reduction these latter bodies very easily give rise to new glycerins. Under the same conditions, the keton-actones can also be decomposed into a mono-basic acid (benzoic acid in the case considered), and an acid which can only be a glycol acid.

Thallium Chlorobromides.—V. Thomas.—The author's experiments show that (1) excess of bromine reacts on thallous chloride in presence of solvents not having any chemical action, to form the chlorobromide, $Th_3Cl_2Br_4$; (2) in presence of solvents—such as carbon disulphide, which are capable of combining with the halogens—thallous chloride is transformed into the bi-bromide, $ThBr_2$. The transformation is total in presence of a sufficient quantity of bromine; (3) in the dry way, the normal addition products of thallous chloride can be obtained. In presence of excess of bromine the chlorobromide, ThClBr, is produced; (4) the apparent displacement of chlorine by bromine ought to be attributed to the formation of intermediate compounds, which are very unstable and capable of reacting with the solvent.

The Reactions of Acetylene with Cuprous Chloride Dissolved in a Neutral Solution of Potassium Chloride.—R. Chavastelon.—The action of acetylene on a saturated neutral solution of cuprous chloride in potassium chloride leads to identical results whether this solution is acid or neutral. In the case of a neutral solution, and one in which the velocity of the gaseous current is not rapid, an active agitation is necessary.

Separation of Cobalt and Nickel by the Electrolytic Method.—Dimetry Balachowsky.—The author's method of separating nickel and cobalt electrolytically consists in the use of a tenth-normal acetic solution of these two metals. To this solution are added 3 grms. of the metal, 3 grms. of ammonia sulphocyanate, 1 grm. of urea, and 1 to 2 c.c. of ammonia, in order to neutralise the excess of acetic acid. The E.M.F. should have a maximum of 1 volt, and the current 0·8 ampère, the temperature of the experiment being 70° or 80°. The time required is about an hour and a half. The nickel and sulphur will be deposited on the cathode, the cobalt remaining in solution. A little nitric acid dissolves up the nickel, and the sulphur can be separated from the dissolved nickel by filtration.

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THE CHEMICAL NEWS.

Vol. LXXXIV., No. 2173.

ON INDUCED RADIO-ACTIVITY PRODUCED BY SALTS OF RADIUM.

By P. CURIE and A. DEBIERNE.

M. and Mdme. Curie have established the fact that when any substance is placed in the neighbourhood of a radiferous salt of barium, it becomes itself radio-active. This induced radio-activity persists long after the removal of the radio-active barium salt; however, it decreases with time, at first rapidly, then more and more slowly, and appears to become asymptotic towards zero. M. A. Debierne has shown that barium salts placed in intimate contact with salts of actinium, temporarily acquire part of the properties of the radiferous salts of barium, and retain this condition for several months. On the other hand, Mdme. Curie has observed, when measuring the radio-activity of oxide of thorium, irregularities which have not yet been explained. M. Owens made the same observations, and showed that the air currents suppress, to a certain extent, a part of the activity of oxide of thorium. M. Rutherford, examining this phenomenon over again, showed that air which had been kept near oxide of thorium and then taken some distance away, retained its conducting power for about ten minutes.

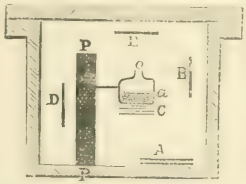

Fig. 1.

He also observed that oxide of thorium was able to produce phenomena of induced radio-activity similar to those caused by salts of radium. Finally, he observed this important fact, that bodies charged with negative electricity are more energetically active than those which are not so charged. M. Rutherford explains these phenomena by admitting that oxide of thorium gives off a particular radio-active emanation susceptible of being carried off by the air and charged with positive electricity by the positive ions in the air. This emanation should be the cause of induced radio-activity. M. Dorn has reproduced, with the radiferous salts of barium, the experiments which MM. Owens and Rutherford made with oxide of thorium. Finally, let us recall the fact that from the commencement of their researches on radio-active bodies, M. and Mdme. Curie were able to obtain, by heating pitchblend, a gas which remained radio-active for a month. (*Comptes Rendus*, Nov., 1899).

We have undertaken a fresh lot of experiments on this induced radio activity, which shows itself under very varied aspects, and of which the nature appears to us to be very far from elucidation.

Radio-activity has been studied by electric means. We quote the following experiments:—1. Induced radio-activity is much more intense when we operate in a closed vessel. The active matter is placed in a small bulb of thin glass, *a*, open at *o*, and placed in the middle of a completely closed vessel (Fig. 1). Various plates, B, D, E, suspended in different parts of the vessel, become active to about the same extent after about one day's exposure. The plate D, placed out of the radiating range behind the lead screen P, P, became as active at B and E. A plate such as A, resting on the bottom, is strongly acted on the exposed side by the air of the box; the face opposite the surface of the box is not sensibly affected. In a series of plates in contact, C, placed close to the bulb, it is only the outer face of the last plate exposed to the air which is strongly acted upon. Every substance appeared to be acted upon in about the same manner (lead, copper, aluminium, glass, ebonite, card, paraffin).

With very active chloride of barium (atomic weight of the metal =174), plates exposed for several days attained an activity 8000 times greater than a plate of metallic uranium of the same dimensions. When exposed to the free air, they lose the greater part of their activity in a day. The activity disappears much more slowly when the plates are left in the closed vessel after having removed the active substance. Finally, if we repeat the above experiments with the bulb *a* completely closed, we obtain no induced activity.

2. The small chamber C (Fig. 2), containing the active body, communicates with the chambers C' and C'', containing the bodies A and B to be acted upon, by means of capillary tubes having an interior diameter of 0·1 m.m., and lengths of 5 c.m. and 75 c.m. The chambers C, C', C'', being very small, the action took place very rapidly and as strongly as if A and B were in the same chamber as the active body.

These phenomena have been observed with various radiferous salts of barium (chloride, sulphate, carbonate). Compounds of actinium also produce induced radio-activity. On the other hand, salts of polonium, even when very active, do not produce any similar effect. As we know, further, that polonium does not emit any rays deviable by the magnetic field, it may be as well to compare these two facts one with the other.

We may conclude from these first experiments, that the radiations from radium do not take any part in the phenomena of induced radio-activity. The only radiations which could interfere would be those extremely absorbable ones which act on the air in immediate contact with the radiant matter.

Induced radio-activity is transmitted in the air through short distances, from the radiant matter to the body to be acted upon; it can also be transmitted through capillary tubes. Bodies are acted upon progressively, the more rapidly as the vessel containing them is the smaller, and they tend towards a limit of induced activity as in the phenomenon of saturation. The limit of activity is the higher as the active body is itself the more active.

Fig. 2.

M. Rutherford's theory of emanation allows of the explanation of these different results; but, as we can

easily conceive other satisfactory explanations, it appears to be somewhat premature to adopt any particular theory just yet. Further, new facts are necessary to settle the question.

However it may be, this phenomenon appears to be one of the most important properties of radio-active bodies. Perhaps it is the necessary complement to deviable radiation.—*Comptes Rendus*, cxxxii., No. 9.

THE NATURE AND ORIGIN OF THE POISON OF *LOTUS ARABICUS*.*

By WYNDHAM R. DUNSTAN, M.A., F.R.S., Director of the Scientific and Technical Department of the Imperial Institute,
and
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THE authors have already given a preliminary account (*Roy. Soc. Proc.*, 1900, vol. lxvii., p. 224), of this investigation, and have shown that the poisonous property of this Egyptian vetch is due to the prussic acid which is formed when the plant is crushed with water, owing to the hydrolytic action of an enzyme, *lotase*, on a glucoside, *lotusin*, which is broken up into hydrocyanic acid, dextrose, and lotoflavin, a yellow colouring matter.

The authors have continued the investigation with the object of ascertaining the properties and chemical constitution of lotoflavin and of lotusin, and also of studying the properties of lotase in relation to those of other hydrolytic enzymes.

Lotusin.

Lotusin can be separated from an alcoholic extract of the plant by a tedious process giving a very small yield, about 0·25 per cent.

Lotusin is a yellow crystalline glucoside, more soluble in alcohol than in water. When heated it gradually decomposes without exhibiting any fixed melting-point. Combustions of specially purified material gave numbers agreeing with those deduced from the formula $C_{28}H_{31}NO_{16}$.

In the preliminary notice the formula $C_{22}H_{19}NO_{10}$ was provisionally assigned to lotusin on the assumption that one molecule of dextrose is formed by its hydrolysis. The formula given above, as the result of ultimate analysis, is confirmed by the observation that two molecules of dextrose are produced by acid hydrolysis, which is therefore represented by the equation :—

$$\underset{\text{Lotusin.}}{C_{28}H_{31}NO_{16}} + 2H_2O = 2\underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Prussic acid.}}{HCN} + \underset{\text{Lotoflavin.}}{C_{15}H_{10}O_6}.$$

When a solution of lotusin is warmed with dilute hydrochloric acid, hydrolysis readily occurs. The liquid acquires a strong odour of hydrocyanic acid, and a yellow crystaline precipitate of lotoflavin is thrown down, whilst the solution strongly reduces Fehling's solution. Dilute sulphuric acid only very slowly effects the hydrolysis of lotusin.

When warmed with aqueous alkalis, lotusin is gradually decomposed, ammonia being evolved, and an acid formed to which the name *lotusinic acid* has been given.

$$C_{28}H_{31}O_{16} + 2H_2O = C_{28}H_{32}O_{18} + NH_3.$$

Lotusinic acid is a monobasic acid furnishing yellow crystalline salts. It is readily hydrolysed by dilute acids, forming lotoflavin, dextrose, and heptogluconic acid (dextrose-carboxylic acid) :—

$$\underset{\text{Lotusinic acid.}}{C_{28}H_{32}O_{18}} + 2H_2O = \underset{\text{Lotoflavin.}}{C_{15}H_{10}O_6} + \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Heptogluconic acid.}}{C_7H_{14}O_8}.$$

With the exception of amygdalin, lotusin is the only glucoside definitely known which furnishes prussic acid as a decomposition product.

* Abstract of a Paper read before the Royal Society, June, 20, 1901.

Lotoflavin.

Lotoflavin is a yellow crystalline colouring matter readily dissolved by alcohol or by hot glacial acetic acid, and also by aqueous alkalis forming bright yellow solutions. It is always present to some extent in the plants, especially in old plants. Ultimate analysis leads to the formula $C_{15}H_{10}O_6$. It is therefore isomeric with luteolin, the yellow colouring matter of *Reseda luteola* and with *fisetin*, the yellow colouring from young fustic, *Rhus cotinus*. *Morin*, from *Morus tinctoria*, appears to be hydroxylotoflavin.

Lotoflavin does not form compounds with mineral acids. It furnishes a tetracetyl derivative and two isomeric mutually convertible trimethyl ethers which are capable of forming one and the same acetyl-trimethyl-lotoflavin. By the action of fused potash lotoflavin is converted into phloroglucin and β-resorcylic acid.

Dextrose.

The sugar resulting from hydrolysis has been found to correspond in all properties with ordinary dextrose.

Hydrocyanic Acid.

The amount of prussic acid given by plants at different stages of growth has been ascertained. Mature plants bearing seed-pods have furnished 0·345 per cent of this acid, calculated on the air-dried material which corresponds with 5·23 per cent of lotusin. Younger plants bearing flower buds gave 0·25 per cent, whilst still smaller quantities were furnished by very young plants, and hardly any by quite old plants from which the seeds had fallen.

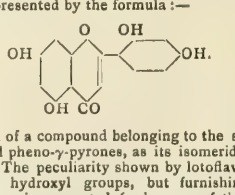
The formation of the poison therefore seems to reach its maximum at about the seeding period, and after this period to diminish rapidly. The Arabs are aware that the plant is safe to use as a fodder when the seeds are quite ripe, but not before. We have found that it is the lotusin which disappears during the ripening of the seeds. Old plants contain some lotase and lotoflavin, but little or no lotusin.

Lotase.

In its general properties lotase resembles other hydrolytic enzymes, from which, however, it differs in several important respects. It may be compared with emulsin, the enzyme of bitter almonds. Emulsin, however, only attacks lotusin very slowly, whilst lotase has but a feeble action on amygdalin, the glucoside of bitter almonds. Lotase is much more readily injured and deprived of its hydrolytic power than emulsin. On this account it is difficult to isolate in the solid state. Its power is not only rapidly abolished by heat, but is also gradually destroyed by contact with alcohol or glycerin. Besides lotase, the plant contains an amylolytic and a proteolytic enzyme.

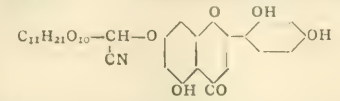
Constitution of Lotoflavin and Lotusin.

Having regard to its reactions, and especially to the production, by the action of fused alkali, of β-resorcylic acid and phloroglucin, the authors conclude that lotoflavin should be represented by the formula :—



which is that of a compound belonging to the same class, of phenylated pheno-γ-pyrones, as its isomerides luteolin and fisetin, The peculiarity shown by lotoflavin of containing four hydroxyl groups, but furnishing only a *tri*methyl ether, is accounted for by one of the hydroxyl groups being in the ortho position to a carbonyl group.

The reactions of lotusin are best represented by the ormula :—



which is that of a lotoflavin ether of maltose-cyanhydrin.

This formula satisfactorily accounts for the partial hydrolysis of the glucoside by alkalis giving lotusinic acid and ammonia, and for the decomposition of the substance by acids giving lotoflavin and maltose-carboxylic acid which is immediately decomposed into dextrose and hepto-gluconic acid. It also accounts for the hydrolysis of lotusin, by acids, into lotoflavin and maltose, which is further changed to dextrose.

In order to definitely localise the position of the cyanogen group in lotusin, the behaviour of several cyanhydrins of known constitution have been examined with reference to the question as to whether they would furnish hydrocyanic acid when acted on by dilute hydrochloric acid. It was found that mandelic nitrile, lævulose cyanhydrin, and pentacetyl gluconitrile, in which the cyanogen group is known to occupy a position similar to that assumed for it in the formula suggested for lotusin, are, like lotusin, easily decomposed by dilute hydrochloric acid forming prussic acid, and the corresponding aldehyde or ketone.

The authors wish again to express their obligations to Mr. Ernest A. Floyer, of Cairo, Member of the Egyptian Institute, who has spared neither trouble nor expense in collecting in Egypt, and despatching to this country, the material required for this investigation.

THE PHARMACOLOGY OF PSEUDACONITINE AND JAPACONITINE CONSIDERED IN RELATION TO THAT OF ACONITINE.*

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In a previous paper on the "Pharmacology of Aconitine and some of its Principal Derivatives" (*Phil. Trans.*, 1898, vol. cxc., p. 239), we have given an account of the physiological action of this, the highly toxic alkaloid of Monkshood (*Aconitum Napellus*), and of its principal derivatives, and we have also discussed the ascertained physiological effects of these substances in relation to their chemical constitution. The results of this investigation have proved to be of much practical importance in connection with the pharmaceutical and medical employment of aconite, especially in demonstrating the partial antagonism to aconitine of benzaconine, and in a greater degree of aconine, both of which derivatives accompany the parent alkaloid in the plant and in the pharmaceutical preparations made from it, which have been hitherto used medicinally. Although it seems likely that these separate alkaloids, and especially aconine, may be useful as therapeutic agents, it is now clear that for the purpose for which aconite is employed, the pure alkaloid, aconitine, should be used in the place of the indefinite mixture of physiologically antagonistic alkaloids contained in pharmaceutical preparations made from the plant.

In a series of papers communicated to the Chemical Society, and published in the *Journal of the Chemical Society* (1891—99), one of us, in conjunction with his pupils, has described the chemical properties of the toxic alkaloid contained in two other species of alkaloid, viz., *Aconitum ferox* or Indian or Nepaul Aconite, and *Aconitum Fisheri* or Japanese aconite. The medicinal employment of these potent drugs has been very restricted in the absence of any definite knowledge as to the nature of their constituents and the physiological action to which they give rise.

Aconitum ferox has long been known to botanists and travellers in India as a poisonous plant of great virulence. It is used in Indian medical practice under the vernacular name of "Bikh." There appear, however, to be several varieties of aconite passing under this vernacular name. This is a subject which we are at present investigating with the assistance of the Government of India.

In 1878 Alder Wright isolated a crystalline, highly toxic alkaloid from the root of the plant, and named it pseudaconitine. In 1897 (*Proc. Chem. Soc.*, 1895, p. 154; *Trans. Chem. Soc.*, 1897, p. 350), one of us gave an account of a complete investigation of the chemistry of this alkaloid, the results of which have led to a modification in certain important respects of the conclusions arrived at by Wright and his co-workers. Our results have been confirmed by Freund and Niederhofheim (*Ber.*, vol. xxix., pp. 6, 852.

For details of the chemistry of pseudaconitine and its derivatives, reference must be made to the paper already referred to (*loc. cit.*). We may here briefly record the chief properties of the alkaloid.

Pseudaconitine is a crystalline alkaloid whose composition differs from that of aconitine, being expressed by the formula $C_{36}H_{49}NO_{12}$. The crystals melt at 202°, and are sparingly soluble in water, but readily in alcohol. The salts are usually crystalline and soluble in water. Their solution and those of the base produce in excessively minute quantities, a persistent tingling of the tongue, lips, and other surfaces with which they are placed in contact, in this respect resembling aconitine and its salts, which produce the same effect.

When heated in the dry state at its melting-point pseudaconitine evolves a molecular proportion of acetic acid, leaving another alkaloid, pyropseudaconitine. This alkaloid, like the corresponding pyro-derivative of aconitine, does not give rise to the characteristic tingling effects of the parent base.

When a salt of pseudaconitine is heated in a closed tube with water, as in the case of aconitine, partial hydrolysis occurs with the loss of a molecule of acetic acid, an alkaloid, veratryl-pseudaconine, being left. This alkaloid, like the corresponding benzaconine, derived by similar means from aconitine, produces neither the tingling sensation nor the toxic effects of the parent base.

The complete hydrolysis of pseudaconitine, which is reached when the above mentioned veratryl-pseudaconine is heated with alkalis, produces, instead of the benzoic acid furnished by aconitine, veratric or dimethylprotocatechuic acid, together with a base, pseudaconine, not susceptible of further hydrolysis. Whilst there is thus a strong general resemblance in chemical constitution between pseudaconitine and aconitine, the benzoic radical of aconitine is replaced in pseudaconitine by the veratric radical of veratric acid, whilst there are probably also constitutional differences in the central nucleus.

The composition and properties of the toxic alkaloid present in Japanese aconite, "Kuza-uzu," regarded by botanists as *Aconitum japonicum* or *A. Fischeri*, has been the subject of some dispute among chemists who have examined it. Wright regarded it as chemically different from aconitine, both in composition and in structure, being an anhydro- or apo-derivative formed by the loss of water and conjugation of 2 molecules of an unknown alkaloid of the aconitine type. He assigned to it the formula $C_{66}H_{88}N_2O_{21}$. Lübbe afterwards studied the properties of japaconitine, and pronounced it to be identical with aconitine, and, more recently, Freund and Beck have reached the same conclusion. Later, one of us, in conjunction with H. M. Read (*Journ. Chem. Soc.*, 1899), subjected japaconitine to a very detailed investigation, in the course of which its properties and those of its principal

* Abstract of a Paper read before the Royal Society, June 20th, 1901.

derivatives were defined and compared closely with those of aconitine. We believe that these results leave little room for doubting that japaconitine is a distinct alkaloid different from aconitine, although Wright was mistaken in the view he took of its composition and constitution. Superficially japaconitine bears a very strong resemblance to aconitine; it is, however, richer in carbon, and the physical properties of its derivatives do not agree with those of aconitine. To this alkaloid we have provisionally assigned the formula $C_{34}H_{49}NO_{11}$, and have retained for it the name of japaconitine suggested by Wright.

In general, the decomposition of japaconitine resembles that of aconitine, but the physical properties of the resulting derivatives are not the same. By the action of heat it furnishes acetic acid and jappyraconitine; on partial hydrolysis, japbenzaconine is obtained besides acetic acid; whilst on complete hydrolysis, the products are acetic acid, benzoic acid, and japaconine. Whilst therefore the constitution of the central nucleus appears to be different, both aconitine and japaconitine contain the acetyl and benzoyl groups, whilst in pseudaconitine the acetyl and veratryl groups are present.

In the present paper the physiological action of specially purified pseudaconitine and japaconitine are recorded and compared with aconitine.

The differences found are nearly always differences of degree and not differences of kind, a result which bears out the close constitutional relationship which is to be inferred from their chemical reactions. Although there are probably constitutional differences in the central nuclei of the three alkaloids, the same constitutional type is to be seen in each, and the substitution of a veratryl group (in pseudaconitine) for an acetyl group (in aconitine) counts for little in influencing the characteristic physiological action.

In order to bring the action of aconitine, pseudaconitine, and japaconitine into a contrast, which may be readily apprehended at a glance, the following summary will be useful:—

Heart.—All three alkaloids have a similar effect upon the heart of such mammals as have been observed. Pseudaconitine is quantitatively more energetic than the other two towards cats, but is certainly not nearly twice as toxic when artificial respiration is practised. Towards the frog's heart pseudaconitine is slightly less powerful than the other two, of which japaconitine is rather the more active.

Vagus Nerve and Inhibitory Mechanism in Heart.—Heart slowing from increased central vagus activity is produced by all these alkaloids, and similar results follow section and stimulation of the nerve at this and later stages of poisoning by one and all of them, both in mammals and frogs.

Respiration.—There is less tendency to acceleration of respiration in mammals poisoned by pseudaconitine than when the other two alkaloids are employed; further the dyspnœal conditions develop more suddenly and the central depression of respiration is greater. Japaconitine is at first slightly more depressant than aconitine, but thereafter the tendency to acceleration of respiration is sooner developed, otherwise the general features of their action are similar.

Blood.—All the aconitines produce a deleterious effect upon the hæmoglobin and coloured corpuscles of the blood when they are given repeatedly in large doses. As far as has been ascertained this is due to impairment in the nutrition of the animal rather than to a direct action.

Frogs kept in a watery medium or in contact with a moist surface, develop œdema after receiving any of the aconitines, but this condition is most marked and the hydræmia of the blood is more pronounced and lasting after pseudaconitine.

Brain and Cord.—All aconitines appear to have a similar effect qualitatively on the brain and cord of rabbits, pigeons, and frogs.

Temperature.—The initial elevation of temperature often seen in rabbits which have received aconitine or japaconitine is less frequently observed after pseudaconitine. A slightly greater and more enduring fall of internal temperature is witnessed after the latter, when the dose is large, and bears a like relationship to the lethal amount.

Repeated Administration.—Some tolerance is established on the part of rabbits towards all the aconitines, and this is manifested with reference to temperature reduction, to the cardiac effect, and, to a lesser extent, to respiration; the general toxicity undergoing a reduction which is not, however, extensive. Less tolerance is shown towards pseudaconitine than towards the other two; it has been found impossible hitherto to determine how far rapidity of elimination varies between the alkaloids.

Sensory Nerves.—Local applications of the aconitine ointments of equal strengths are followed by a somewhat more powerfully depressant and enduring effect when these contain aconitine or japaconitine than pseudaconitine. This statement has reference to cutaneous sensory and thermic impressions in the human subject. The difference is at most but slight.

Motor Nerve and Muscle.—The action of the individual alkaloids is much the same whether specimens of *R. esculenta* or *R. temporaria* are used. It is more difficult to reduce reaction or to produce insensitiveness of the intramuscular motor nerves by pseudaconitine than by the other alkaloids. The so-called curare-like action has been found for all the alkaloids to be much feebler than was at one time supposed.

Direct contact of the alkaloidal solutions with muscle-nerve preparations reduces excitability, the muscle being affected by solutions containing less than 1 in 1,000,000, and the nerve by solutions still weaker. Pseudaconitine is recognised as producing a rather weaker effect than the two other alkaloids, which are nearly equal to one another, japaconitine being slightly the more energetic.

The results of the experiments detailed in this paper do not in all respects agree with previous observations; especially is this the case with regard to the relative toxicities of the three aconitines. The general order of toxicity towards mammals is pseudaconitine, japaconitine, and aconitine, which is the least toxic. Pseudaconitine has been found (roughly speaking) twice as toxic as aconitine towards the small mammals and birds used in the research. This agrees closely with the results of Adelheim (*Forens. Chem. Untersuch*, Dorpat, 1860), and Böhm and Ewers (*Arch. f. Exp. Path. u. Pharm.*, 1873, Bd. 1, s. 385). Clotta (*Lehbr. d. Arzneim. u. Arzneiverordnungis*, Freib., 1885), states that pseudaconitine is the stronger alkaloid, but gives no proportion. Our results differ from those of Nothnagel and Rossbach (*Mat. Med. u. Therap.*, Fr., 1880, 685), who state that pseudaconitine is seventeen times as active as aconitine, and of Harnack and Meunicke (*Berl. Klin. Wchsch.*, 1883, No. 43, s. 657), who find the under margin of active dosage equal. Kobert (*Lehbr. d. Intox.*, s. 657), finds pseudaconitine and aconitine to be in activity "ziemlich gleich."

The relative toxicity of japaconitine to aconitine is approximately as ten to about nine towards the small mammals and birds which were used. Previously, japaconitine has been seldom contrasted with the other two aconitines, but has been recognised as stronger than aconitine by Langaard (*Arch. f. Path. Anat.*, 1880, lxxix., s. 229), and in one series of observations by Harnack and Meunicke. Kobert, on the other hand, does not separate japaconitine from aconitine and pseudaconitine in toxicity.

Dosage.—Based upon the observations made, the relative doses for therapeutical purposes would be approximately, regarding that for aconitine as the unit, for pseudaconitine 0·4 to 0·45, and for japaconitine 0·8.

Towards frogs the toxicity of these alkaloids is by no means so great (per grm. body-weight), as it is towards the same unit of the mammals and birds included in this research. Thus the lethal dose per kilo. mammalian weight may only be lethal to 140 to 170 grms. of frog weight, or even to less, according to the time of year. A medium-sized rabbit may therefore be poisoned by a dose

of aconitine or japaconitine which would suffice to destroy six or eight frogs.

Japaconitine is slightly more toxic towards both mammals and frogs than is aconitine, but the higher toxicity of pseudaconitine towards birds and mammals is not associated with an equal activity towards frogs, for it exerts towards both *R. esculenta* and *R. temporaria* a slightly lower toxicity than do either of the other alkaloids.

There is no essential difference in the reaction of *R. esculenta* and *R. temporaria* respectively to individual aconitines beyond a greater or less accentuation of one or other symptom, as for example more excited movement in the latter, more reduction of reflex in the former, but in all parallel series of observations the resistance of *R. esculenta* has proved to be slightly greater to all the aconitines examined.

As concerns the local action of the aconitines upon sensory (cutaneous) structures in man, the differences are so trifling as to be negligible.

As regards the therapeutical employment of aconitine, japaconitine, and pseudaconitine, the great similarity in their physiological actions, amounting almost to a qualitative identity which is established by this investigation, justifies the employment of any one for internal administration, provided that the dosage is properly regulated. Given in the just proportions mentioned above, the three alkaloids would exert the same action. We strongly recommend the use of a pure alkaloidal salt in preference to preparations made from the plants, since the latter would be difficult to standardise, and even if this were done, the action of the aconitines would be modified to a greater or less extent by the other alkaloids present in the vegetable preparation.

For local applications the three alkaloids may be introduced into ointments in identical proportions. The greater toxicity of pseudaconitine need not prevent its use in this department of treatment if it is remembered that all applications of the aconitines, externally, are to be considered dangerous if any abrasion of the skin is present.

The chemical part of this inquiry has been conducted in the Laboratories of the Scientific Department of the Imperial Institute, with the assistance and co-operation of the Government of India. Our thanks are specially due to Dr. George Watt, C.I.E., Reporter on the Economic Products to the Government of India, for the interest he has shown in the investigation, and for the care he has taken in the collection of the necessary material.

The physiological experiments have been conducted in the Department of Materia Medica and Pharmacology of the University of Aberdeen, and have been assisted by a grant made by the Royal Society from the Government Fund. The assistance of Drs. Esslemont and Fraser has been very valuable in carrying out some of the observations entailed in this department of the research.

"MOHAWKITE."

By JOSEPH W. RICHARDS.

Dr. Kœnig has given the name Mohawkite to the nickeliferous and cobaltiferous variety of domeykite found at the Mohawk mine. He bases this on his analyses, corresponding to $(Cu,Ni,Co)_3As$ (*Am. Journ. Sci.*, December, 1900; *Zeit. fur. Krystallographie und Mineralogie*, 1901, xxxiv., 70).

Dr. Ledoux published the results of an analysis of a mineral from the same mine (*Engineering and Mining Journal*, April 7, 1900), which corresponded closely to $(Cu,Ni,Co)_4As$, and which he proposed should be called Mohawkite. Dr. Kœnig, however, throws doubt upon the formula obtained by Ledoux; also claims that if Cu_4As does exist, a new name must be found for it, as he has preempted the name Mohawkite for his variety of domeykite. The object of this communication is to substantiate Ledoux's analysis and formula, and thereby prove the existence of the new species $(Cu,Ni,CO)_4As$.

Last autumn the writer received from Foote, of Philadelphia, a specimen from the Mohawk mine marked "*Mohawkite?*" Analysis of the material, completely freed from gangue, gave—

	Per cent.
Copper	70·8
Cobalt	6·4
Nickel	trace
Iron	0·0
Arsenic (by difference) ..	22·8
	100·0

The atomic ratios from the above are—

Copper	$\frac{70·8}{63·4} = 1·117$	1·225
Cobalt	$\frac{6·4}{59} = 0·108$	
Arsenic	$\frac{22·8}{75} =$	0·304

Hence, the atomic ratio $\frac{1·225}{0·304} = 4·003$ and the formula $(Cu,Co,Ni)_4As$.

Dr. Ledoux's analysis, as calculated by Kœnig, gives the corresponding atomic ratio $\frac{1·228}{0·302} = 4·066$. Kœnig, however, makes a slight mistake in adding the basic valencies, and the correspondence is still closer. I have re-calculated Ledoux's results, as follows:—

	Atomic ratios.	
Copper	68·6	1·082 } 1·218
Cobalt	1·2	0·020
Nickel	6·55	0·112
Iron	0·23	0·004
Sulphur	0·53	0·017
Arsenic	22·67	0·302

Assuming the sulphur to be present as RS, we subtract its ratio 0·017 from that of the bases, and there remains 1·201. Ledoux's ratio is therefore $\frac{1·201}{0·302} = 3·98$.

I would propose the name *Ledouxite* for the compound Cu_4As, the existence of which no longer appears doubtful. It carries small percentages of cobalt and nickel and is similar in appearance to algodonite, with density 7·8 (Ledoux) or 8·07 (Richards). The latter was taken on clean material free from gangue.—*American Journal of Science*, xi., p. 457.

EXPERIMENTS ON CHALCOPYRITE.*

By LEONARD P. MORGAN and EDGAR F. SMITH.

At various times experiments have been made in this laboratory looking to the determination of the constitution of certain natural chemical products. Thus, the state of oxidation of the iron in pyrite, marcasite, and arsenopyrite has received considerable attention, and in the present communication it is desired to give the results of similar experiments made upon the mineral chalcopyrite. Weighed portions of the latter were exposed in porcelain boats to the action of dry hydrochloric acid gas. As the mode of procedure has been sufficiently detailed in former papers, it may be omitted here. It will suffice to note that the heat was obtained from a single Bunsen burner with a wing top. The period of heating covered one hour, beginning of course with a gentle heat, and increasing finally to a full red heat. The boat and contents

* Contribution from the John Harrison Laboratory of Chemistry. From the *Journal of the American Chemical Society*, xxiii., No. 2.

were allowed to cool in the gas. On their withdrawal from the tube they were placed in a beaker containing distilled water. The combustion tube was also washed out carefully with water. The aqueous solution of the iron salt was strongly diluted, acidified with sulphuric acid, and the liquid titrated with potassium permanganate.

Results.

	Chalcopyrite. Grm.	Iron found. Grm.	Iron found. Per cent.
1.	0·2112	0·06489	30·72
2.	0·2039	0·06231	30·56
3.	0·2007	0·06164	30·70
4.	0·1996	0·06128	30·67
5.	0 2089	0·06398	30·63
6.	0·2140	0·06553	30·62

In several instances the liquid in the receiver placed at one end of the combustion tube showed traces of ferric iron when the thiocyanate test was applied. This might readily occur when it is remembered that the quantity of ferrous chloride thus volatilised was exceedingly small, and that its exposure during the time required for the completion of the experiment would be enough to cause its oxidation. However, the quantity of ferric iron was extremely small.

The formula generally assigned the mineral is $CuFeS_2$, which would require 30·5 per cent of iron. The results given above therefore indicate a complete decomposition of the material by hydrochloric acid, and also show that all of the iron is in the ferrous state. This proved to be the case with marcasite. As hydrochloric acid gas does sometimes act as a reducing agent, there was a possibility that perhaps it might have transformed any ferric iron present in the mineral into the ferrous condition. To render the results as certain as possible, portions of the mineral were carefully heated in sealed tubes with a solution of copper sulphate, as had been done with marcasite. The evidence gathered in this way corroborated the first experience, and it can safely be asserted that chalcopyrite contains all of its iron in the ferrous form, and that the mineral is, perhaps, nothing more than a substituted marcasite, in which copper has replaced its equivalent of iron.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JUNE 30TH, 1901.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, July 10th, 1901.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 200 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from June 1st to June 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 200 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The deficiency of rain has been still further accentuated during the past month; the actual rainfall at Oxford was 1·52 inches, of which half, *i.e.*, 0·75 inch, fell on the 30th. The average fall for June during the past thirty-five years is 2·10 inches; this leaves a deficit of 0·58 inch, and brings the total deficit for the year to 2·30 inches, or 21·2 per cent.

Our bacteriological examinations of 516 samples have given the results recorded in the following table; we have also examined 57 other samples, from special standpipes, &c., making a total of 573 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	204
New River, filtered (mean of 125 samples) ..	8
Thames, unfiltered (mean of 25 samples) ..	1371
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 279 samples)..	26
Ditto ditto .. .. highest	260
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 25 samples) ..	488
River Lea, from the East London Company's clear-water wells (mean of 37 samples) ..	56

Of the 441 samples of impounded and filtered water supplied to London, examined bacteriologically during the past month, thirty-six samples, or 8·1 per cent, were sterile. Ten samples out of the total number examined contained more than 150 microbes, and twenty-six samples, or 5·8 per cent, contained more than 100 microbes per c.c. The mean of the microbes in the excess samples was 155, against a corresponding mean last month of 147, showing that the quality of the water remains substantially the same as it was in the month of May.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

CONTRIBUTIONS TO THE SCIENCE OF NITROCELLULOSE.*

By G. LUNGE and J. BEBIE.

INTRODUCTION. (Nitration of Cellulose, Methods of Determination). A. Influence of Water on the progress of Nitration. B. Influence of Sulphuric Acid on the progress of Nitration. C. The highest attainable degree of Nitration of Cellulose by means of Nitro-sulphuric Acid. D. The solubility of Nitrocellulose in Ether-alcohol. E. Formula of Kisniemsky. F. Influence of the amount of Nitrous Acid contained in the Nitric Acid upon the percentage of Nitrogen, and the gain of Nitrocellulose. G. Influence of Nitrous Acid contained in the Nitric Acid upon the stability of Gun-cotton. H. Influence of Nitration with a higher proportion of Water upon the stability of Gun-cotton. I. Relative behaviour of different kinds of Cotton on Nitration, specially with regard to the production of Collodion-cotton. K. Examination of marketable varieties of Collodion-cotton ("soluble" Nitrocellulose for Explosive Gelatin and Art Silk. L. The behaviour of Nitrocellulose in Polarised Light. M. Colouration of Nitrocelluloses with Iodine..

INTRODUCTION.

Stages of Nitration of Cellulose.—As the molecular weight of cellulose is not known, the number of theoretically possible stages of nitration must be left undecided. Conversely, attempts have been made to establish the

* *Zeitschrift für Angewandte Chemie*, 1901, Heft 20.

molecular weight of cellulose from the nitrocelluloses actually prepared. If this could not supply an absolute value, yet at least it afforded a fundamental value for the cellulose formula.

Eder was able to prepare four different stages of nitration from the maximum, which formerly was said to be "trinitrocellulose," as far as "mononitrocellulose," and he therefore doubled the formerly accepted cellulose formula, $C_6H_{10}O_5$ to $C_{12}H_{20}O_{10}$.

Vieille obtained, between the same limits, eight different stages of nitration, which he described as tetra- to endeca-nitrocellulose. The "hexa-nitrocellulose" of Eder, which he would name "dodecanitrocellulose," he was unable to obtain, but only a stage of nitration lying between hexa- and penta-; a further reason for him to assign to cellulose the formula $C_{24}H_{40}O_{20}$.

Mendeleeff succeeded in preparing a nitrocellulose with 12·44 per cent nitrogen, soluble in ether-alcohol. This stands midway between the deca-nitrocellulose, shown by Vieille to be insoluble, and the soluble ennea-nitrocellulose, and is considered by him as a distinct compound. But such a half-way stage between the ninefold and tenfold nitrated cellulose is excluded by the formula $C_{24}H_{40}O_{20}$. Mendeleeff, therefore, doubled the formula again, and traced back the stages of nitration from $C_{48}H_{80}O_{40}$.

It appeared in the course of this research that a soluble form of the deca-nitrocellulose also exists; hence, from the solubility alone of Mendeleeff's product no reason can be deduced for establishing the last named formula.

It is true that $C_{24}H_{40}O_{20}$ certainly does not correspond to the actual size of the cellulose molecule, but as nothing certain is known concerning the latter, and the formula $C_{24}H_{40}O_{20}$ suffices to characterise the hitherto known stages of nitration, it might be advisable for reasons of simplicity to retain this formula provisionally. These and other reasons to be mentioned later inclined us to retain Vieille's classification and nomenclature. Unless specially mentioned, therefore, the nitration stages of the following always depend upon the formula $C_{24}H_{40}O_{20}$. The French chemists give the results of the nitrogen determination regularly in c.c. of nitric oxide reduced at 0° and 760 m.m., which are evolved from 1 grm. of the substance; while in Germany and England the proportion of nitrogen is mostly expressed in percentages. Hence a comparison of both designations is given in the following table:—

Name.	Formula.	C.c. NO from 1 grm.	Percentage N.
Nitrocellulose—			
Dodeca- ..	$C_{24}H_{28}O_8(NO_3)_{12}$	226·27	14·14
Hendeca- ..	$C_{24}H_{29}O_9(NO_3)_{11}$	215·17	13·47
Deca-	$C_{24}H_{30}O_{10}(NO_3)_{10}$	203·35	12·75
Ennea- ..	$C_{24}H_{31}O_{11}(NO_3)_9$	190·75	11·96
Octo-	$C_{24}H_{32}O_{12}(NO_3)_8$	177·19	11·11
Hepta- ..	$C_{24}H_{33}O_{13}(NO_3)_7$	162·36	10·18
Hexa- ..	$C_{24}H_{34}O_{14}(NO_3)_6$	145·93	9·15
Penta- ..	$C_{24}H_{35}O_{15}(NO_3)_5$	127·91	8·02
Tetra-	$C_{24}H_{36}O_{16}(NO_3)_4$	107·81	6·76

The nitration stages from tetra- to deca-nitrocellulose can be obtained by means of nitric acid alone; to obtain a higher proportion of nitrogen mixtures of nitric and sulphuric acids are necessary. For the production of nitrocelluloses on a large scale, mixtures of both acids are used for all the stages of nitration; therefore this method of nitration has been used almost exclusively in the present work.

We have subjected the most important factors which come into play during the process of nitration to a more exact examination, and in connection with this have confirmed the conditions which are necessary for the production of the different stages of nitration. We naturally cannot tell whether much in the information here given is not already known, and does not come into the consideration of those not initiated into such secrets of manufacture.

A few extra methods of determination may next be added.

Determination of the Nitrogen.—For this purpose the products were dried in the apparatus described by Lunge and Weintraub. The drying was then conducted at a temperature of 40°; but since, according to our observation, a slight decomposition of the sulphuric acid usually takes place at 40°, we endeavoured to avoid even this trace of decomposition, although it might not affect the results. Nothing of the kind was ever noticed at 30—32°, and it was therefore always dried at this temperature.

The nitrogen determinations were carried out in the Lunge nitrometer. The decomposition of the nitrocellulose in concentrated sulphuric acid could in most cases be carried out in the funnel of the decomposition vessel itself, only with a few short fibred products this was performed in special weighing glasses. The time of decomposition is also dependent on the physical activity of the material. As long as the structure of the cellulose is preserved, only a short time is usually necessary for complete solution. On the contrary, compact products, which offer little surface to the sulphuric acid, may require as much as twenty hours. But the use of the swan-neck funnel, used long ago by Lunge for this purpose, excludes every possibility of loss. Concentrated or slightly diluted sulphuric acid may be used for cleaning out the funnel. According to Williams the use of the latter makes the results about 0·2 per cent higher. He traces this to the rise of temperature caused by the mixture of the diluted with the concentrated sulphuric acid, and concludes that without this, *i.e.*, by using concentrated sulphuric acid alone, the decomposition is incomplete. We were not able to confirm this. Comparative analyses showed the same results by using concentrated as by using diluted sulphuric acid.

Also, after treating with concentrated acid alone, the residue, after the evolution and absorption of nitric oxide, upon further treatment with diluted acid, gave no more evolution of gas, which must be the case if Williams's assumption were correct.

The results obtained by the comparison just mentioned are here added because they afford a proof of the great accuracy of this method. All our determinations vary seldom more than 0·3 c.m. per 1 grm., *i.e.*, about 2/100.

Washing out with—	C.c. NO per 1 grm.	Percentage N.	Mean.
Concentrated sulphuric acid	212·15	13·302	13·290
	211·78	13·278	
Diluted acid	211·70	13·273	13·382
	211·98	13·291	

Determination of the Solubility in Ether-alcohol.—Two methods are in use for this determination. In the one the product is treated for some time with ether-alcohol, the insoluble portion filtered off, washed, dried, and weighed. But in this manner accurate results can only be obtained when only a small proportion of soluble material is present. Otherwise the collodion solution is difficult to filter, and in consequence a thorough washing of the insoluble part is impossible.

In these cases the other method (the so called English prescription) must be used. In this the nitrocellulose is treated with a certain quantity of ether-alcohol in closed cylinders. After the insoluble portion has settled, an aliquot part of the clear liquid above is drawn off in a pipette, evaporated, and dried at 50° till the weight is constant. The collodion thus separates out as an adhesive mass, which is with difficulty completely freed from ether-alcohol. In consequence of this the results obtained are too high. With completely soluble products 102—103 per cent was generally found. An attempt was therefore made to separate the nitrocellulose in a finely divided flocculent form; this was attained by adding water before evaporating, and stirring well till there was a permanent milkiness. In this way accurate results were obtained.

(To be continued).

AN IMPROVED METHOD OF PRODUCING ULTRA-VIOLET SENSITIVE PLATES.*

By V. SCHUMANN.

It is a known fact that the sensitiveness and intensity of the gelatin dry plate decrease considerably from the wavelength 220 $\mu\mu$ towards the shorter waves. I have already demonstrated that the cause of this decrease lies in the insufficiency of transparency of the gelatin. Silver bromide itself gives rise to no such decrease of sensitiveness, nor does this happen when working with very small quantities of gelatin.

Upon this fact was based my former method of producing ultra-violet sensitive plates, which enabled me to investigate the rays beyond 185 $\mu\mu$. This method had its drawbacks, as I did not fail to point out at the time. I have been occupied till quite recently in obviating these drawbacks.

In this manner I have gradually obtained a plate which essentially supersedes the original in purity, in reliability, and in delicacy of gradation in the intensity. With this plate I am now carrying out my observations of the spectrum *in vacuo*, with growing success.

In its fundamental features the improved method may be represented as follows:—A silver bromide gelatin emulsion very rich in silver is prepared, allowed to stiffen, washed, and dissolved in much water, then filtered and poured upon flat glass plates, upon which the silver bromide is deposited. Half-an-hour afterwards the emulsion is poured off again. The fine film of silver bromide which remains on the plate dries, on account of its thinness, in a very short time. Immediately after drying the plate can be used for photographic purposes.

Still better results are obtained if the heavier particles of silver bromide are removed from the emulsion before filtering. The formation of the film requires in this case several hours.

Preparation of the Emulsion.—In detail the method is as follows:—9 grms. potassium bromide, 4·5 grms. gelatin (Nelson I.), and 60 c.c. distilled water are placed in a beaker of about ½ litre capacity; further, 11·25 grms. silver nitrate and 60 c.c. distilled water in a boiling flask of ½ litre capacity; and 20 to 30 minutes later, after which time the gelatin is sufficiently swollen, both are placed in a water-bath at 50 to 60° C., in which they remain until the melting of the gelatin is complete.

Then, using the brown, or red dark-room light, the silver solution is passed in a thin stream, or in small portions, into the gelatin solution, continuously shaken, and, after closing the beaker, its contents are vigorously shaken.

The vessel is now placed for half an hour in a water-bath of 60° C., after which its contents are carefully poured out into a porcelain basin, so that the deposit of silver bromide remains behind as far as possible. The basin is placed in the cold (not above 4° C.), or upon ice, when the emulsion is sufficiently stiffened in two to three hours. The firmer the emulsion becomes the more easily is it broken up, this being a necessary prelude to the washing.

The emulsion, cut up into small pieces with a horn spatula, is heaped up in the middle of a piece of muslin, which is then fastened together into a bag. The bag is allowed to hang for two or three hours in running water, or, if this is not convenient, in a deep glass holding at least 2 litres, which is filled with water not above 14° C. After changing the water ten times at intervals of a quarter of an hour, the dissolved salts ($KBr.KNO_3$), whose removal is to be effected, are washed out. The bag is now taken out of the bath, lightly pressed to remove the water adhering to the gelatin, and then hung in a glass beaker of 1½ litre capacity, which contains 950 c.c. freshly boiled out water, cooled down to 55° C. The emulsion dissolves in it in a few minutes. It is gently stirred with a glass rod, and then twice filtered through glass-wool (which is firmly plugged 1 c.m. deep in the tube of the funnel), into a clean beaker. The layer of wool must be of such a thickness that the emulsion only runs through slowly. The formation of bubbles must here be avoided more carefully than before by stirring with the glass rod. This is best assured by allowing the emulsion to flow from the mouth of the funnel down the side of the flask in a constant stream.

After filtering, the emulsion is immediately poured upon the glass plates, which will be presently described.

It has been shown that plates of this kind are liable to surface faults, which are apparent before development as streaks and numerous dark spots, and which develop simultaneously with the picture on plates that have been kept for some time before usage. In cases where these spots are objectionable it is best to remove from the emulsion the coarser of the silver bromide particles which it always contains in varying sizes. This can be done by pouring out the dissolved emulsion before it is filtered, into a basin with a flat bottom, and allowing it to stand for three quarters of an hour. In this manner the heavier silver bromide, which seems to favour the formation of spots, is deposited, and fine particles, which yield purer and more reliable films, remain behind in the liquid. But the deposition in the basin only answers its purpose when the layer of liquid for the stated time of deposition is correspondingly thin. I obtained the best results from a layer 4 to 5 m.m. thick.

Preparation of the Glass Plates.—The glass plates require a different preparation from ordinary photographic plates, if they are to hold, without danger of spilling, the unusually large quantity of very liquid emulsion required for the formation of the sensitive film. If one desired to use the ordinary photographic glass plate, the emulsion would overflow before it had been poured on in any quantity. This does not happen if the sharp edges of the plate are ground away. This is most easily done by means of coarse particles of emery—emery paper is less well-adapted for the purpose—which are laid upon, or firmly fastened to, a smooth foundation. The glass plate, inclined (30°) to the emery surface, is scraped upon this until a rough face of about ½ m.m. breadth is uniformly produced in place of the sharp edge. This breadth is immaterial; the principal point is, that the sharp edge of the plate shall be everywhere converted into a rough surface, otherwise the untouched parts give an easy outlet for the overflow of the emulsion.

After this the plates are dipped for an hour or longer in nitric acid, washed with water, dried with a clean cloth, polished, and dusted. It is advisable to polish shortly before covering the plates. If a longer time elapses between the two operations, the emulsion flows less well, as the plates very readily re-absorb gases.

Before covering, the plates are laid side by side at a distance of from 1 to 2 c.m., upon a long, narrow, level plate of mirror glass, which stands on feet about 8—10 c.m. high. For convenience later, when the emulsion is to be poured on, it is advisable to let the plates project on the side of the operator with their long side 2 to 3 cm. over the edge of the mirror.

(To be continued).

* *Annalen der Physik*, 1901, vol. v.

Vacancies.—Applications are invited for the following Appointments:—Lecturer in Chemistry at the Borough of Swansea Municipal Technical College; salary £200—250. Assistant Lecturer and Demonstrator in Agricultural Chemistry at the University College of North Wales, Bangor; salary £120.

The Dialcoylamidobenzylbenzoic Acids. Derivatives of the Benzoylised Acids.—A. Haller and A. Guyot.—The authors describe the preparation and properties of dimethylamidobenzylbenzoic acid, diethylamidobenzylbenzoic acid, ethylbenzylamidobenzylbenzoic acid, dimethylamidometaoxybenzylbenzoic acid, diethylamidometaoxybenzylbenzoic acid.—*Bull. Soc. Ch.*, No. 4.

AMMONIUM AMALGAM.

Coehn (*Ztschr. Anorg. Chem.*, xxv., 430) has recently, published the results of an investigation on this subject, and these are given here in abstract. The increase in volume which takes place during the formation of ammonium amalgam has been used as an argument in favour of the view that ammonia and hydrogen are absorbed as such by the mercury, and that a distinct substance, ammonium, is not in combination with the mercury. In opposition to this view it has been shown that the volumes of the gases evolved bear to each other the ratio $NH_3 : H = 2 : 1$; and further, that neither ammonia nor hydrogen is absorbed by mercury.

An attempt has been made by Landolt to obtain some experimental evidence of the metallic nature of the substance ammonium, contained in the amalgam, by bringing the freshly prepared amalgam into solutions of salts of the heavy metals and determining whether, under these conditions, ammonium can replace these metals from their salts. Treated in this manner, neither copper, nor silver, nor iron, could be precipitated. This, he says, is opposed to the view that ammonium has a metallic nature.

Le Blanc thought it possible that the ammonium might be so unstable that it would not have the power to replace metals, but would decompose into ammonia and hydrogen as soon as liberated from the amalgam.

He attempted to solve the problem as to the nature of the substance contained in the amalgam by electrolysing solutions of ammonium salts, using a mercury cathode, and comparing the polarisation on the one hand with that which results when an alkali amalgam is formed in this way, and, on the other, with that which is obtained when hydrogen alone is developed on the cathode. If the value found approximates that obtained by electrolysing an alkali salt it would argue in favour of the existence of ammonium in the amalgam. If, on the contrary, it approached the value when hydrogen alone is developed on the cathode, it would argue against the existence of ammonium. His results pointed to the existence of ammonium in the amalgam.

It has been shown that in addition to the tension at which the development of hydrogen takes place in a reversible manner, as in platinised platinum, there is a characteristic tension for each metal. Thus, the reversible evolution of hydrogen, obtained by discharge of hydrogen on a mercury cathode with continuous current, took place at 1·52 volts. If an alkali metal is in solution, using the mercury cathode, there is obtained in addition to the point at 1·52 volts another point beneath this, which changes with the nature of the alkali metal, and is, therefore, characteristic of the latter, and corresponds to the formation of the amalgam. This took place with ammonium at 1·24 volts, and is therefore completely analogous to the case of the alkali metals.

The only argument against the metallic nature of ammonium still remaining was that of Landolt, and it is this which Coehn has tested in a different manner and under different conditions. The ammonium amalgam was freshly prepared by electrolysis and dropped into a solution containing copper sulphate. A platinum wire which was connected through a galvanometer with a platinum plate suspended in the solution projected upward through the bottom of the vessel. The amalgam came in contact with the platinum point, and the action of the element, if copper is replaced, would be to deposit copper on the plate, with the simultaneous passage of a current through the galvanometer. It was found that no copper was deposited, and only a weak current of momentary duration passed through the galvanometer. To test whether Le Blanc was correct in supposing that ammonium was too unstable to replace other metals, he prepared the amalgam so that it would be more stable by electrolysis of ammonium salts, cooled down nearly to 0°.

It was found that the amalgam thus prepared did not show the tendency to swell up unless it was warmed, and it has quite a metallic appearance. When ammonium amalgam, thus prepared, was brought into a solution of copper sulphate, cooled to about the same temperature, the formation of copper amalgam could be seen with the naked eye. Observing these precautions and using the apparatus mentioned above, separation of copper on the plate took place at once.

That the replacement is not due to the hydrogen developed by the decomposition of the ammonium is shown by the fact that metals like cadmium, and especially zinc, which are not reduced by hydrogen, can be precipitated in this way from solutions of their salts.

The author has thus removed the last experimental evidence against the metallic nature of ammonium.—*American Chemical Journal*, xxv., No. 5.

THE DENSITY AND MOLECULAR WEIGHT OF OZONE.

Since Soret's (*Liebig's Ann. Chem.*, cxxxviii., 145; and Suppl., V., 148) celebrated work on the density and molecular weight of ozone, carried out more than thirty years ago, no work has been done on this subject until Ladenburg (*Ber. d. Chem. Ges.*, xxxi., 2508) took it up in 1898. Soret worked with a mixture of ozone and oxygen containing only 5 per cent. of ozone, and hence Ladenburg deemed it important to re-determine these values, using purer ozone.

The ozone which he used was generated in a Siemens ozoniser, whereby a mixture of ozone and oxygen was obtained containing 8 to 9 per cent. of the former, which could be easily liquefied in liquid air. The author liquefied such a mixture by means of liquid air, and then allowed the mixture to boil until most of the oxygen had boiled off. A new mixture of liquid ozone and oxygen was addue to the residue, and again the oxygen was allowed to boil off. By repeating this operation several times he succeeded in obtaining 2 to 3 c.c. of a blackish-blue, non-transparent liquid. He determined the density of the gas obtained when this liquid was vaporised and also the percentage of ozone in it. The density was determined by measuring the time of escape of the gas from a Schilling's apparatus and comparing it with the time of escape of pure oxygen from the same apparatus. The apparatus had been previously tested with pure oxygen and nitrogen, and was found to give very satisfactory results.

Ladenburg thus found that the gas under investigation required 430 seconds to escape, while pure oxygen required 367 and four-tenths seconds. Hence, the density of the gas was 1·3698, that of oxygen being 1. The percentage of ozone in the gas was determined by titrating, the iodine liberated from a solution of potassium iodide by a known volume of the gas. It was thus found that the gas contained 86·16 per cent. by weight of ozone. From these data the density of pure ozone was calculated to be 1·456, that of oxygen being 1, while theoretically it should be 1·5.

Soon after the publication of these results Ladenburg (*Ber.*, xxxi., 2830) published a note in which he made a correction. In the calculations by which the above results were obtained, he really assumed the molecular weight of ozone to be 48, while this is what he was trying to prove. So he deduced two algebraic equations, which, when solved, gave him 84·4 per cent. by weight as the percentage of ozone in his mixture of ozone and oxygen, and 1·469 as the density of pure ozone.

Shortly after this Staedel (*Ber.*, xxxi., 3143) and Gröger (*Ber.*, xxxi., 3174) published, at about the same time, criticisms of Ladenburg's work, in which their chief objection was that it is impossible to calculate the density of pure ozone when the density of a mixture of oxygen

and ozone and the amount of iodine liberated from potassium iodide only are known. Staedel claimed that Ladenburg assumed ozone to be O_3, and that in one of his equations he assumed the action of ozone on potassium iodide to consist in one atom of the oxygen in ozone liberating two atoms of iodine from the potassium iodide, an assumption which he had no right to make, since he was trying to determine whether ozone is O_3. Gröger expressed the belief that it would be possible to determine the density of ozone only when some absorbent was used which would absorb the ozone entirely without leaving behind a volume of oxygen equal to the volume of ozone started with.

In answering these two criticisms Ladenburg (*Ber.*, xxxii., 221) agreed with Staedel and Gröger that the molecular weight of ozone cannot be determined from the density of a mixture of ozone and oxygen and the amount of iodine liberated by such a mixture, but he did not agree that this fact detracted from the value of his results.

He again called attention to the fact that the ozone prepared by him was nearly pure. After the oxygen had boiled off at −186° from the liquid mixture of ozone and oxygen, the thermometer rose 60° without any gas being evolved. The determination of the density of his ozone, which contained a little oxygen, gave the value 1·3698, which corresponds to a molecular weight of 43·8. This showed conclusively, Ladenburg thought, that the molecule of ozone is O_3. If, for instance, it were O_4, there would be an error in his results of over 50 per cent., and the conclusion would follow that his ozone contained 60 per cent of oxygen, for which there was not the slightest evidence.

The determination of iodine liberated from potassium iodide was made merely to ascertain the percentage of ozone in his mixture, which was found to be 84·4 per cent. This value was then used in correcting the density found to that of pure ozone and 1·469 was the result obtained, which corresponds to a molecular weight of 47.

Quite recently Brunck (*Ber.*, xxxiii., 1832), in an article on the quantitative determination of ozone, referred again to the apparently inadequate proof of Ladenburg that ozone has the molecular weight 48. This reference called forth another reply from Ladenburg (*Ber.*, xxxiii., 2282), in which he used substantially the same argument which he used against Staedel and Gröger, and further he criticises some of the results of Brunck regarding the liberation of iodine from potassium iodide in acid solution. Brunck (*Ber.*, xxxiii., 2999) answered these criticisms in a later paper.—*American Chemical Journal*, xxv., No. 5.

ON THE METEORIC STONES WHICH FELL NEAR ZOMBA, BRITISH CENTRAL AFRICA, ON JANUARY 25TH, 1899. WITH NOTES ON THE CHEMICAL ANALYSIS OF SUCH BODIES.*

By L. FLETCHER, M.A., F.G.S.,
Keeper of Minerals in the British Museum.

(Continued from p. 19).

Determination of Chromite: Absence of Diamond.

6. The same residue was treated finally with hydrofluoric and sulphuric acids. The insoluble material was transferred to a watch-glass, and microscopically examined; as it was entirely opaque and of metallic lustre, no diamond could be present; after ignition it weighed 0·0035 grm., and gave the reactions of chromium. The above number corresponds to 0·35 per cent of chromite in the unattracted material; but it is only a minimum, for part of the chromite, being very finely divided, would probably yield to the attack of the acid, and be carried into solution.

Determination of Sulphur and Phosphorus: Absence of Titanium.

7. 0·9920 grm., treated in the way described in a previous paper (*Mineralogical Magazine*, 1894, vol. x., p. 298), yielded $BaSO_4$ 0·1481, and $Mg_2P_2O_7$ 0·0024. During these operations it was ascertained that titanium was absent.

Determination of the Alkalis.

8. 0·4815 grm., analysed by the Lawrence-Smith method, gave:—Sodium and potassium chlorides, 0·0135; tested with a small spectroscope, only the sodium line was visible; K_2PtCl_6 (free from filter), 0·0040; adherent to filter and ignited, 0·0036.

A blank experiment simultaneously made with the same reagents gave:—Sodium and potassium chlorides, 0·0021; K_2PtCl_6 free from filter), 0·0056; adherent to filter and ignited, 0·0012.

Treatment with Mercuric Solution.

9. 4·9856 grms. were treated with mercuric solution in an atmosphere of hydrogen, as already described; the extraction proceeded for twenty-four hours and was performed three times. The first extract was appreciable; the second and third showed only slight tinges of colour.

The combined extracts yielded:—

CuS (ignited in air), 0·0003.

After oxidation of the iron and decomposition of the ammonium chloride, the residue was green, showing its comparative richness in nickel; the solution gave—

Fe_2O_3,SiO_2 0·0025, yielding SiO_2 0·0004.

NiO 0·0007.

CaO 0·0040, probably almost entirely due to the action on the glass and porcelain during the precipitation of the iron and the removal of the nickel.

$Mg_2P_2O_7$ 0·0037.

Treatment with Hydrochloric Acid and Sodic Solution: First Portion.

10. 2·5065 grms. of that part of the unattracted material which had not been subjected to the action of the mercuric solution were extracted three times with dilute hydrochloric acid, according to the method described in a previous paper (*Mineralogical Magazine*, 1894, x., p. 302). In this case the extracts were decanted from the undecomposed material (admixed with free silica), and the decanted liquid and the undecomposed material separately evaporated to complete dryness; the continued action of the acid on the main material during the evaporation was thus prevented, though a certain amount of action on the finely-divided silicate suspended in the liquid cannot be avoided. The free silica was next extracted with strong solution of sodium carbonate (to which a piece of caustic soda had been added); in the last stages of the washing of the undecomposed material a little of the finely-divided silicate passes through the pores of the filter; the amount of this was afterwards determined. The sodic extract was examined, not only for silica, but for bases.

The following numbers were obtained:—

a. Undecomposed material.—Part washed from filter, 0·9186; part adherent to filter and ignited, 0·1328.

b. The acid solution yielded:—

Fe_2O_3,Al_2O_3,SiO_2 0·4639; of this 0·4150, after the iron had been expelled by the Deville-Cooke method, gave Al_2O_3,SiO_2 0·0055, and from this 0·0019 of SiO_2 was obtained.

MnS 0·0068.

NiO 0·0001.

The rest of the acid solution, containing the calcium and magnesium, was lost.

c. The sodic solution yielded:—

SiO_2, with trace of undecomposed material, 0·4909. After treatment with HF and H_2SO_4 and subsequent ignition, 0·0039. The residue thus obtained was partly reddish and partly white; the

* From the *Mineralogical Magazine*, vol. xiii., No. 59, 1901.

former was oxide of iron, the latter was found to contain magnesium; the residue was thus due to the trace of undecomposed material which had passed through the pores of the filter.

$Fe_2O_3,Al_2O_3\ SiO_2$ 0·0048, yielding SiO_2 0·0031, and the Fe_2O_3, as judged from the colour, being small.

CaO 0·0020, partly due to action on the vessels.

Treatment with Hydrochloric Acid and Sodic Solution: Second Portion.

11. 2·7333 grms. of the unattracted material, which had been subjected to the action of the mercuric solution (§ 9) and still contained mercury and mercurous chloride, treated in the above way with hydrochloric acid, gave the following:—

a. Undecomposed material.—Part washed from filter, 1·0981; part adherent to filter and ignited, 0.0516.

b. The acid solution yielded.—

Fe_2O_3,Al_2O_3,SiO_2 0·5013; of this 0·4169 gave Al_2O_3,SiO_2 0·0044, which yielded SiO_2 0·0028.

MnS 0·0074.

NiS (after ignition in air) 0·0012.

(CaO, due to action on the vessels, 0·0022).

CaO 0·0105 (in all the analyses the calcium was twice precipitated).

SiO_2 0·0061 was obtained after the decomposition of the ammonium chloride by nitric acid, and is a measure of the amount of action on the vessels.

$Mg_2P_2O_7$ 1·3834.

c. The sodic solution yielded:—

SiO_2, with trace of undecomposed material 0·5301.

After treatment with HF and H_2SO_4 and subsequent ignition, 0·0017.

Fe_2O_3,Al_2O_3,SiO_2 0·0065; of this 0·0046 gave Al_2O_3,SiO_2 0·0032, which itself yielded SiO_2 0·0007.

CaO 0·0013 (probably due, in part at least, to the action on the glass and porcelain).

d. Another portion, weighing 2·0583 grms., lost 0·0512 of volatile material when heated, in a current of hydrogen, in a platinum boat contained in a platinum tube supported in an oven at 298° C.; at this low temperature the troilite remains unaffected.

Treatment with Hydrochloric Acid and Sodic Solution: Third Portion.

12. 2·0317 grms. of the unattracted material, which had been subjected to the action of the mercuric solution (§ 9), but from which the volatile material had been removed by heating at a low temperature in a current of hydrogen, gave the following numbers:—

a. Undecomposed material.—Part washed from filter, 0·8107; part adherent to filter and ignited, 0·0241.

b. The acid solution yielded:—

Fe_2O_3,Al_2O_3,SiO_2 0·3775; of this 0·3352 gave Al_2O_3,SiO_2 0·0018, and the latter when analysed yielded Al_2O_3 0·0001, SiO_2 0·0016.

CuS (ignited in air) 0·0003.

MnS 0·0056.

Ni(Co) 0·0010.

CaO 0·0107.

SiO_2 0·0067 was obtained after the decomposition of the ammonium chloride by nitric acid, and is a measure of the amount of action on the vessels.

$Mg_2P_2O_7$ 1·0958 (and this includes the calcium and aluminium due to the action of the nitric acid on the porcelain dish).

c. The sodic solution yielded:—

SiO_2, with trace of undecomposed material, 0·4208. After treatment with HF and H_2SO_4 and subsequent ignition, 0·0026.

Fe_2O_3,Al_2O_3,SiO_2 0·0069; of this 0·0047 gave Al_2O_3,SiO_2 0·0022, and the latter when analysed gave Al_2O_3 0·0024, SiO_2 0·0001.

(CaO, due to action on porcelain dish, 0·0012).

(To be continued).

CORRESPONDENCE.

ESTIMATION OF AMMONIA IN ITS SALTS.

To the Editor of the Chemical News.

SIR,—In my letter which appeared in the CHEMICAL NEWS of June 21st (vol. lxxxiii., p. 299) I placed on record the results of a few experiments which proved that, by boiling a solution of an ammonium salt with a slight excess of N/5 Na_2CO_3, a quantitative decomposition takes place, and the ammonia can thus be indirectly estimated.

It is plain to every "chemist" that, if the sample in which the ammonia is to be estimated is acid, it must first be exactly neutralised with Na_2CO_3, and then a known quantity of N/5 Na_2CO_3 added. In the same way, if alkaline, it must be neutralised with acid before the estimation is proceeded with.

No doubt there are cases where this method would be useless; *e.g.*, in highly coloured solutions it would be absurd to use an indicator.

Difficulties of this nature would be foreseen by a trained chemist, and he would alter his process accordingly.

A correspondent, Mr. McIntosh, in your issue of July 5th (CHEM. NEWS, vol. lxxxiv., p. 10), mentions that by this simple process he would return a sample of supposed ammonium sulphate wholly adulterated with acid sulphate of soda as containing 15 per cent of NH_4. I think this quite possible; in fact, from the letter of July 5th more than probable. Working on the same lines it would be possible to find a certain percentage of NH_4 in a sample of pure dilute sulphuric acid.

I should be pleased to hear privately from any of your readers who have applied this method to the estimation of ammonia in commercial ammonium sulphate, manures, &c.—I am, &c.,

M. BENNETT BLACKLER.

Finsbury Technical College,
July 13, 1901.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxii., No. 25, June 24, 1901.

Chemical Equilibrium. Reactions of Two Bases placed simultaneously in presence of Phosphoric Acid.—M. Berthelot.—The author investigates the reactions of two bases placed simultaneously in presence of phosphoric acid. These reactions can be divided into three fundamental cases, according to the sum of the valencies of the bases which tend to unite with one molecule of acid. This sum may be equal to one valency, R, as PO_4RH_2; to two valencies, R_2, as PO_4R_2H; or to three valencies, R_3, as PO_4R_3.

Acetylo-metallic Radicles.—M. Berthelot.—A new compound can be obtained by the action of acetylene on cuprous chloride in hydrochloric solution, which corresponds to the formula $C_2H_2Cu_2Cl_2$; this, however, may be written $(C_2H_2Cu)Cl.CuCl$, and is a double chloride of cupros-acetyl, corresponding to the double argentacetyl iodide and the double cupros-acetyl iodide—substances which have already been prepared.

Synthesis of a Coloured Derivative of Diphenylene-phenylmethane.—A. Haller and A. Guyot.—The authors' present researches are an attempt to solve the following problem:—Being given a coloured derivative of triphenylmethane (as, for example, crystalline violet), what modifications occur in the properties when this substance is transformed into the ortho-product of the two phenylic radicles in a coloured derivative of phenyl-fluorene?

Action of an Oxide or a Metallic Hydrate on the Solutions of Salts of other Metals; Mixed Basic Salts.—Paul Sabatier.—In a paper recently published in the *Comptes Rendus*, M. Recoura announced that he obtained directly, by contact of cupric hydrate with certain metallic salts, mixed basic salts; and he described a certain number of these compounds. The author draws attention to the fact that some time ago he undertook researches on the action of oxides or metallic hydrates produced in saline solution, and he prepared a whole series of mixed basic salts analogous to those isolated by M. Recoura.

Preparation of Phosphorous Oxide.—A. Besson.—The author prepares phosphorous oxide by dissolving hydrobromic acid gas in pure cold phosphoryl chloride; through this a stream of PH_3 gas passes. The formation of phosphonium bromide is accompanied by the deposition of a small quantity of a yellowish solid. By gently raising the temperature above 50°, and keeping the whole on a water-bath for some hours, a voluminous orange precipitate forms, which can be separated out by filtration. This, after purification, was analysed and found to possess the formula P_2O.

Action of Solar Radiation on Chloride of Silver in presence of Hydrogen.—M. Jouniaux.—When powdered silver chloride is exposed to sunlight in an atmosphere of pure hydrogen, it soon loses its white colour, gradually becoming black after passing through a series of intermediate tints. Under these conditions metallic silver is formed, at least on the surface of the particles of chloride, and it is found that hydrochloric acid gas is produced. The author finds the relative proportions of these substances after varying periods of time.

Action of Mercuric Oxide on Aqueous Solutions of Metallic Salts.—A. Mailhe.—In a preceding paper, the author examined the action of mercuric oxide on salts of zinc, nickel, cobalt, and copper. He now continues his researches on this subject, and considers the action of mercuric oxide on salts of manganese, cadmium, lead, ferrous salts, and ferric salts.

Action of Bases and Acids on Amine Salts.—Albert Colson.—The author has already established the fact that piperidine gives, in contact with ammoniacal salts, a reaction limited by the tension of the ammonia gas. He now publishes some actual measurements of tensions, and shows that the reversibility of the reaction presents peculiarities analogous to those which have been stated with regard to the dissociation of silver carbonate.

Racemic Erythrite.—L. Maquenne and G. Bertrand.—The authors' researches confirm the accuracy of the results announced by M. Griner in 1893, and also discover the specific properties of inactive erythrite by compensation. The fusion-points of the four stereoisomers of erythrite, together with those of their characteristic derivatives, are shown in the following table:—

	Free tetrites.	Tetra-acetine.	Acetals. Valeric.	Acetals. Benzoic.
Inactive erythrite	+120°	+85°	Liquid	+202°
Racemic erythrite	+72°	+50—51°	+72—73°	+220°
Active erythrite	+88°	Liquid	+105—106°	+231°

The family of the tetrites is thus found in the same way as that of the pentites, defined in all the possible theoretical terms.

Action of Acid Chlorides on Aldehydes in presence of Zinc Chloride.—Marcel Descudé.—The author investigates the reaction of acetyl chloride on trioxymethylene, and of benzoyl chloride on trioxymethylene.

Nitration of Acetylacetic Ethers and of their Acidyle Derivatives.—L. Bouveault and A. Bongert.—In a preceding research, the authors prepared the two methyl butyrylacetylacetates, and decomposed them under the influence of water and the alkalis. They now subject these two substances to the action of fuming nitric acid, and examine the products in both cases.

Acidimetric Value of Parasulphanilic Acid.—G. Massol.—Parasulphanilic acid is interesting on account of its proximity to the aromatic amine function of the mineral acid group. The acid used in the author's experiments was white and well crystalline; it volatilised without melting. The acidimetric value, using phenolphthalein, gives 100·5 per cent calculated on the formula $C_6H_4.NH_2.SO_3H$. The product is therefore anhydrous.

TO CORRESPONDENTS.

A. Bairstow.—The experiment seems to be a very simple one; why not try it?

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PATENTS, DESIGNS, AND TRADE MARKS ACTS, 1883 TO 1888.

NOTICE IS HEREBY GIVEN that George William Johnson, of 47, Lincoln's Inn Fields, in the County of London, has applied for leave to amend the Specification of Letters Patent No. 24748 of 1899, granted to him for "Improvements in the Manufacture or Production of Sulphuric Anhydride and means to be employed therein."

Particulars of the proposed amendment were set forth in the "Illustrated Official Journal" (Patents) issued on the 10th July, 1901.

Any person or persons may give Notice of Opposition to the Amendment (on Form G), at the Patent Office, 25, Southampton Buildings, London, W.C., within one calendar month from the date of the said Journal.

C. N. DALTON,
Comptroller-General.

JOHNSONS & WILCOX,
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47, Lincoln's Inn Fields,
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THE CHEMICAL NEWS.

Vol. LXXXIV., No. 2174

ON THE SEPARATION OF THE LEAST VOLATILE GASES OF ATMOSPHERIC AIR, AND THEIR SPECTRA.*

By G. D. LIVEING, M.A., Sc.D., F.R.S.,
Professor of Chemistry in the University of Cambridge,
and
JAMES DEWAR, M.A., LL.D., F.R.S.,
Fullerian Professor of Chemistry, Royal Institution, London.

Our last communication to the Society (*Roy. Soc. Proc.*, vol. lxvii., p. 467), related to the most volatile of the atmospheric gases; that which we now beg leave to offer relates to the least volatile of those gases. The former were obtained from their solution in liquid air by fractional distillation at low pressure, and separation of the condensible part of the distillate by cooling it in liquid hydrogen. The latter were, in the first instance, obtained from the residue of liquid air, after the distillation of the first fraction, by allowing it to evaporate gradually at a temperature rising only very slowly. The diagram, Fig. 1, will make the process intelligible. A represents a vacuum-jacketed vessel, partly filled with liquid air, in which a second vessel, B, was immersed. From the bottom of B a tube, *a*, passed up through the rubber cork which closed A, and from the top of B a second tube, *b*, passed through the cork and on to the rest of the apparatus. Each of these tubes had a stopcock, *m* and *n*, and the end of tube *a* was open to the air. A wider tube also passed through the cork of A, and led to an air-pump, whereby the pressure above the liquid air in A was reduced, and the temperature of the liquid reduced by the consequent evaporation. To keep the inner vessel, B, covered with liquid, a fourth tube, *r*, passed through the cork, and its lower end, furnished with a valve, *p*, which could be opened and closed by the handle, *q*, dipped into liquid air contained in the vessel C. As the

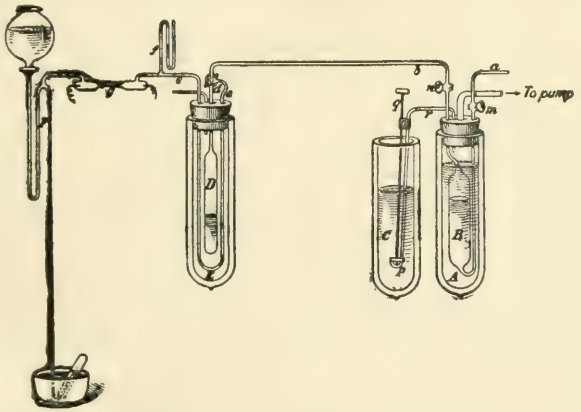

Fig. 1.

pressure above the liquid in A was less than that of the atmosphere on opening the valve, *p*, some of the liquid air was forced through *r* into A by the pressure of the atmosphere, and in this way the level of liquid in A maintained at the required height.

Since B was maintained at the temperature of liquid air boiling at reduced pressure, the air it contained condensed on its sides, and when the stopcock *n* was closed and *m* opened, more air passed in through the open end of *a*, and was in turn condensed. In this way B could be filled completely with liquid air, the whole of the most volatile gases being retained in solution in the liquid.

The tube, *b*, passing from the top of B, was connected with a three-way stopcock, *d*, by which it could be put in communication with the closed vessel, D, or with the tube *e*, by which also D and *e* could be connected. The tube *e* passed down nearly to the bottom of the vacuum-jacketed vessel E, and out again through the cork; and on to a gauge *f*, and through a sparking tube *g* to a mercury pump F. The stopcock *n* being still closed, the whole of the apparatus between *n* and the pump, including the vessel D, was exhausted, and liquid hydrogen introduced into E. The three-way cock, *d*, was then turned so as to connect *c* with D, and close *e*, and then *n* opened. B was thereby put in communication with D, which was at a still lower temperature than B, and the gas dissolved in

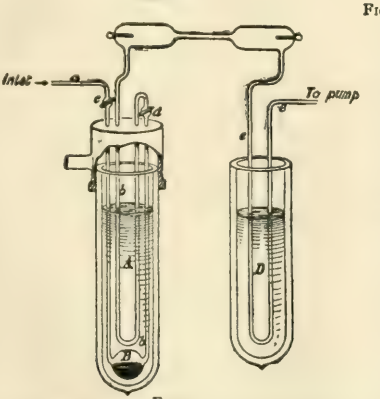

Fig. 2.

* A Paper read before the Royal Society, June 20, 1901.

the liquid in B, along with some of the most volatile part of that liquid, distilled over, and the latter condensed in a solid form in D. When a small fraction of the liquid in B had thus distilled, the stopcock *d* was turned so as to close the communication between D and *c*, and open that between D and *e*. Gas from D passed into the vacuous tubes, but in so doing it had to pass through the portion of *e* which was immersed in liquid hydrogen, so that condensible matter carried forward by the stream of gas was frozen out.

For separating the least volatile part of the gases the vessel E, with its contents, was dispensed with, and the tube *c* made to communicate directly with that connected with the gauge, sparking tube, and pump; and generally several sparking tubes were interposed between the gauge and pump, so that they could be sealed off successively. The bulk of the liquid in B consisted of nitrogen and oxygen. These were allowed gradually to evaporate, the temperature of B being still kept low so as to check the evaporation of the gases less volatile than oxygen. When a great part of the nitrogen and oxygen had thus been removed, the stopcock *n* was closed, and the tubes partially exhausted by the pump, electric sparks passed through *g*, and the gases examined spectroscopically. More gas was then evaporated from B, and the spectroscopic examination repeated from time to time.

The general sequence of spectra, omitting those of nitrogen, hydrogen, and compounds of carbon, which were never entirely removed by the process of distillation alone, was as follows:—The spectrum of argon was first noticed, and then as the distillation proceeded the brightest rays, green and yellow, of krypton appeared, and then the intensity of the argon spectrum waned, and it gave way to that of krypton until, as predicted by Runge, when a Leyden jar was in the circuit, the capillary part of the sparking tube had a magnificent blue colour, while the wide ends were bright pale yellow. Without a jar the tube was nearly white in the capillary part, and yellow about the poles. As the distillation proceeded, the temperature of the vessel containing the residue of liquid air being allowed to rise slowly, the brightest of the xenon rays began to appear, namely, the green rays about λ 5420, 5292, and 4922, and then the krypton rays soon died out, and were superseded by the xenon rays. At this stage the capillary part of the sparking tube is, with a jar in circuit, a brilliant green; and is still green, though less brilliant, without the jar. The xenon formed the final fraction distilled.

Subsequently an improved form of apparatus was used for the fractionation. It is represented in Fig. 2. A gas-holder containing the gases to be separated, that is to say, the least volatile part of atmospheric air, was connected with the apparatus by the tube *a*, furnished with a stopcock *c*. This tube passed on to the bulb B, which in turn communicated through the tube *b* and stopcock *d* with a sparking tube, and so on through the tube *e*, with a mercurial pump. (The Sprengel in figure is simply diagrammatic). Stopcock *d* being closed and *c* opened, gas from the holder was allowed to pass into B, maintained at low temperature, and there condensed in the solid form. Stopcock *c* was then closed and *d* opened, and gas from B allowed to pass into the exhausted tubes between B and the pump. The tube *e* was partly immersed in liquid air in order to condense vapour of mercury, which would otherwise pass from the pump into the sparking tube. The gas passing into the sparking tube would, of course, have a pressure corresponding to the temperature of B, and this was further ensured by making the connecting tube pass through the liquid in which B was immersed. The success of the operation of separating all the gases which occur in air, and which boil at different temperatures, depends on keeping the temperature of B as low as possible, as will be seen from the following consideration.

(To be continued).

THE PHARMACOLOGY OF PYRACONITINE AND METHYLBENZACONINE CONSIDERED IN RELATION TO THEIR CHEMICAL CONSTITUTION.*

By J. THEODORE CASH, M.D., F.R.S.,
Regius Professor of Materia Medica in the University of Aberdeen,
and
WYNDHAM R. DUNSTAN, M.A., F.R.S.,
Director of the Scientific Department of the Imperial Institute.

In a previous paper (*Phil. Trans.*, 1898, pp. 190, 239), we have shown that an entire change in the physiological action ensues on the withdrawal of the acetyl group from aconitine as is seen in the action of benzaconine, the first hydrolytic product of aconitine, from which it differs in containing an atom of hydrogen in the place of one acetyl group. This alkaloid is devoid of the characteristic physiological action and extraordinary toxicity of aconitine, whilst in respect of its action on the heart it is in the main antagonistic to that of the parent alkaloid. In order to study further the remarkable dependence of the physiological action on the presence of the acetyl group we have examined the action of two derivatives of aconitine which we have obtained in this research, viz., pyraconitine and methylbenzaconine.

Pyraconitine was first prepared by one of us (Dunstan and Carr, *Trans*, *Chem. Soc.*, 1894, vol. lxv., p. 176), by heating aconitine at its melting-point, when the acetyl group is expelled as one molecule of acetic acid, and the alkaloid pyraconitine remains. This compound therefore differs in composition from aconitine by the loss of one molecule of acetic acid, and from benzaconine by one molecule of water.

Methylbenzaconine was obtained from aconitine by heating it with methyl alcohol in a closed tube (*Proc. Chem. Soc.*, 1896, p. 159). A remarkable reaction takes place, in which the acetyl group is ejected as acetic acid, a methyl group taking its place. This alkaloid therefore differs from aconitine in containing a methyl group in the place of the acetyl group, and from benzaconine in containing a methyl group in the place of one atom of hydrogen. The examination of its physiological action would therefore be the means of studying the result of replacing in aconitine the negative radical acetyl by the positive methyl group, and also of studying the effect of the introduction of methyl in modifying the physiological action of benzaconine.

The acetyl group of aconitine evidently occupies an exceptional position in the molecule of aconitine. So far as we are aware, it is the only acetyl compound at present known which exchanges this group for methyl when it is heated with methyl alcohol. We have examined the behaviour of numbers of different types of acetyl derivatives from this point of view, and can find none analogous to aconitine.

For the study of their physiological action these alkaloids have been specially purified and employed as hydrobromides in aqueous solution.

Contrasting the physiological action of pyraconitine with that of aconitine, as described in the present paper, we find, as might be anticipated from our previous results, that through the removal of the acetyl group the great toxicity of aconitine is nearly entirely abolished, and the characteristic features of aconitine poisoning are no longer produced by pyraconitine.

Contrasting the physiological actions of benzaconine and pyraconitine which differ from each other empirically by one molecule of water, pyraconitine, the anhydride, is the more active compound. Both these alkaloids, divested of the acetyl group of aconitine, are relatively weak, and feebly toxic when compared with the parent alkaloid.

Although benzaconine and pyraconine exhibit a strong similarity in the physiological effects they produce, there are differences between them which are probably more

* Abstract of a Paper read before the Royal Society, June 20, 1901.

considerable than they would be if pyraconitine were merely the anhydride of benzaconine.

The substitution in aconitine of methyl for acetyl which occurs in the formation of methyl benzaconine has led to a very considerable reduction in toxicity, and has introduced a curare-like effect similar to that first observed by Crum Brown and Fraser (*Trans. Roy. Soc. Ed.*, 1869, vol. xxv., 192), to result from the introduction of methyl into the molecule of an alkaloid. Methyl benzaconine is, however, more toxic and generally more powerful than benzaconine, owing to the presence of the methyl group.

Action of Pyraconitine.

The main effects of pyraconitine may be thus summarised. Its local application is devoid of the effects characteristic of the aconitines. Its chief action upon the heart is to cause slowing, partly from vagus irritation, partly from depression in function of intrinsic rhythmical and motor mechanisms.

There is less tendency to want of sequence in the cardiac chamber walls than is observed after the aconitines and benzaconine.

The vagus apparatus remains active in degree after doses somewhat in excess of the lethal, the slowed heart of pyraconitine being accelerated both by vagotomy and by atropine.

Activity of respiration is reduced (by central depression) to a degree incompatible with life, as is the case after aconitine and benzaconine. The peripheral motor nerves and muscular tissues are not at this time markedly affected. Artificial respiration prolongs life, but the slowed heart and greatly reduced blood pressure tend to a fatal issue.

The spinal cord is impaired in its reflex function, apparently secondarily to reduced circulation in its structure. A tendency to tonic spasm in frogs is late in appearing, and of moderate degree. It has not been seen after destruction of brain and medulla. It is further associated with a curious condition of exaggerated motility.

Neither muscular nor intramuscular nervous tissue are strongly influenced by pyraconitine in lethal or somewhat hyperlethal doses. The lethal dose per kilo. frog's weight is practically about twelve times that which is lethal per kilo. rabbit's weight.

Contrasted Effects of Pyraconitine and Benzaconine.

Of these two alkaloids, pyraconitine is approximately six to seven times more toxic towards mammals (rabbits and guinea-pigs) than benzaconine, and five to six times more so towards frogs. They are alike in their action upon mammals, in so far as they are non-irritant, that they slow the respiration without preliminary acceleration, that they slow the heart and reduce the blood pressure to a very low level, that they cause paresis, and in guinea-pigs clonic movements, and that respiratory failure is the immediate cause of death. They differ in so far that pyraconitine acts more rapidly, but for a shorter period, whilst fatal termination of poisoning is preceded by convulsions, which are very rare after benzaconine. Benzaconine alters the sequence of the ventricles upon the auricles much more usually and to a greater extent than pyraconitine, though if asequence is developed it has the same general character (the auricular second beat being blocked from the ventricle).

Whilst pyraconitine stimulates the cardiac vagus both centrally and within the heart and finally occasions only a limited reduction in its activity, benzaconine produces but little stimulation, and ultimately suspends the vagus inhibitory action. Under these conditions atropine is, of course, inoperative. Both accelerate the heart in small, but slow it in large, dose, and both may disorder the sequence, but vagus inhibition is much more interfered with by benzaconine. Frogs poisoned by benzaconine lose the power of voluntary movement, then reflex disappears, and finally the circulation is arrested; but after pyraconitine, reflex outlasts the heart's action. Late spasm occurs after the latter, not after the former. Whilst in lethal doses pyraconitine has no effect beyond somewhat favouring fatigue and reducing excitability of motor nerves, benzaconine greatly impairs their function, and in thorough poisoning may suspend it entirely.

Action of Methylbenzaconine.

The action of methylbenzaconine may be summed up as follows:—It is very feeble in its toxicity when contrasted with aconitine, but is somewhat stronger than benzaconine.

Small and medium doses, whilst slowing the heart, do not cause any failure in sequence, but larger doses have this effect. They act upon the rhythm of the organ, involving the movement of the auricle and ventricle, whilst ultimately the sequence of the latter upon the former is impaired, so that it follows only a certain proportion of the auricular "leads." This block is not removed by atropine. Whilst the passage of the ventricle into the diastole is at first retarded, the contractile power of the myocardium is ultimately reduced by methylbenzaconine.

The cardiac vagus is depressed in action and its inhibitory function is ultimately suspended by large doses, neither section of the vagus nor atropine administration relieving the slow and faulty action of the organ.

There is evidence of slight primary stimulation of reflex cord centres when ligature of vessels prevents the masking of this condition by the peripheral action of the poison. The subsequent impairment in cord reflexes is later in occurring and of much shorter duration than the action of methylbenzaconine upon intramuscular motor nerves.

In mammals the paralytic symptoms are predominant, the fall of temperature is in part attributable to this cause as well as to changes in the circulation. The clonic movement and salivation (observed in a certain stage of the action of methylbenzaconine, especially upon guinea-pigs) are suggestive of the action of a near ally of aconitine. In frogs, however, there is no semblance to an aconitine effect, unless its very feeble action towards sensory nerves or its much more powerful action upon motor nerves, be thus viewed. Motor nerves are greatly affected by doses which are distinctly below the lethal for cold-blooded animals, the action being curare-like in character. Muscular tissue is after the action of large doses more susceptible of fatiguing influences. Fibrillation in muscles to which the poison has access is more common than after aconitine or any other derivative examined.

These observations support in the main the contention of Crum Brown with Fraser that the introduction of methyl into the molecule of certain spasm-producing alkaloids, marks the effect of these by occasioning a curare-like action at the periphery.

Contrasted Effects of Methylbenzaconine and Aconitine.

The toxicity of aconitine is, roughly, eighty to one hundred times that of methylbenzaconine towards rabbits and guinea-pigs, and much the same proportion holds for summer and winter frogs respectively. Whilst slight tendency to salivation and retching movements are produced by methylbenzaconine, and are in so far suggestive of a slight aconitine action, the absence of initial acceleration of respiration, of local irritation, and dyspnœal convulsions, and the predominance of paralytic symptoms, are points of difference. The action upon the heart is entirely distinct, for the pulse is slowed by methylbenzaconine, the auricles eventually beating more rapidly than the ventricles, the action of the poison proceeds uniformly and without the intermissions which characterises aconitine, whilst the early phenomena of vagus stimulation have little in common. The general symptoms of poisoning in frogs have scarcely a point of similarity, quiescence, rapid failure of reflex, and voluntary movement, without impairment of the cardiac action, are distinctive of methylbenzaconine, whilst excitement with great motility and persistence of voluntary movemen

follow aconitine. Fibrillation is much more pronounced after the former, though it is only a transitory phenomenon. The action on the heart differs widely in frogs as it does in mammals, whilst the curare-like action of the derivative on motor nerves is not produced by aconitine in doses which just suffice to arrest the heart.

It is true that large but sublethal doses of aconitine are followed by a condition of almost complete paralysis, which lasts for several days, but during this time there is slight voluntary and reflex movement, the nerve-endings are not put out of action, and the circulation is usually of the feebiest character, all conditions which are not found in the period of quiescence following methylbenzaconine.

Contrasted Effects of Methylbenzaconine and Benzaconine.

Methylbenzaconine is from three to four times more toxic towards rabbits and guinea-pigs than benzaconine, and from twice to thrice as toxic towards frogs (*R. temp.* and *R. esc.*). In mammals, slight salivation, retching movements, and muscular tremor are characteristic effects of the former, but dyspnœa, ataxia, and paresis are also seen after benzaconine. Of the two, methylbenzaconine is distinctly less depressant towards the heart. Slowing of the pulse and want of sequence of ventricular upon auricular action occurs after both, but is a much earlier symptom after benzaconine, which causes more disorder in the motor mechanism. On the other hand, the intracardiac vagus is put out of function more readily by methylbenzaconine. Death after either poison is rarely preceded by spasm. Neither of the two compounds cause any local irritation in frogs, but methylbenzaconine produces active fibrillation in the muscles, to which it gains access and develops a complete curare-like action much more prominently than does benzaconine, the heart continuing to beat strongly. Benzaconine, in dose sufficient to cause such an effect at the periphery, acts disastrously upon the circulation. In partial poisoning by methylbenzaconine the characteristic rapid failure of the intramuscular motor nerves on stimulation is well marked, but the subsequent recovery on resting, so characteristic of benzaconine, has not been observed.

AN IMPROVED METHOD OF PRODUCING ULTRA-VIOLET-SENSITIVE PLATES.*

By V. SCHUMANN.

(Continued from p. 32).

Covering the Plates.—This must be performed as soon as possible after laying the plates on the level mirror glass and filtering the emulsion. One pours over little plates immediately out of the supply-flask, which is held with its opening very near the receiving surface to avoid the formation of bubbles; with larger plates the quantity of emulsion for each plate is measured off. In the first case the emulsion is poured on till the plate is covered with it —50 to 60 c.c. are necessary for plates 13×18 c.m. For the plates for my own use—which measure only 9×13 c.m.—I need 25 c.c. One must always endeavour to cover the nearer corners, those on the side of the operator, before the further ones, for sometimes the emulsion flows slowly, and does not reach all the corners. Then, instead of adding an excess of emulsion, it is better to assist the covering of the corners by carefully and gradually raising the opposite side of the plate. And this is more readily carried out on the near side than on the other. Whilst doing this, one must avoid disturbing the edge, and should rather press against the underside of the mirror.

Deposition of Silver Bromide for Formation of the Sensitive Film.—The covered plate must be protected from dust during the hours of deposition of the silver bromide; it is also advisable to check as far as possible all evaporation, so as to preserve the original concentration of the emulsion. I attain both objects by covering the mirror glass, on which the plates stand, with a large pasteboard box covered on the inside with shellac varnish, and excluding all light. The temperature of the room, during formation of the film, should not be below 18° C. In three to four hours there is a sufficient deposition of silver bromide. There is a supernatant layer of emulsion, poor in silver, and of milky aspect, which can be poured off without detriment to the film. This is the only part of the whole process which demands special attention in order to secure a successfully prepared plate.

To Pour off the Emulsion.—This is conducted in the following manner, always beginning with the first plate on the left, the glass mirror being in front of the operator:—The plate is now pushed out over the nearest (left) edge of the supporting surface, till about $\frac{1}{10}$ of its length projects. Beneath this is placed a deep evaporating dish, which is 1 to 2 c.m. wider than the plate. If the plate is now raised from beneath with the first finger of the left hand, high enough for it to turn about the margin of the mirror plate, its free end sinks into the dish, whereby the emulsion flows off over both corners, and one can take hold of the plate by the edges of the raised corners, remove it, and stand it up to dry upon a board covered with blotting-paper, and bearing a row of vertical wooden rods, against which the plate leans with the film side downwards. In pouring off the emulsion and placing the plates on the drying board, the plates should be held to prevent the formation of streaks, so that the emulsion flowing along the edge cannot trickle across the silver bromide coating. The streaks thus confine themselves to the immediate neighbourhood of the margin, and may be cut away, but which do not affect the larger plates.

To Dry the Film.—The drying of the plate may be carried out in a room free from dust, or in a drying cupboard. The latter is preferable as the film is very sensitive to air currents, which produce zones of drying, and these show themselves in the negative as varying intensity in the film and noticeable lines. The tendency to formation of zones is greater in this film, which dries very quickly, than in the ordinary gelatin dry plate. A quarter of an hour is sufficient for drying under some circumstances. In my dry cupboard, which in this case I do not ventilate, these plates require from half to three quarters of an hour. If the plate is required for exposure as soon as possible it may without hesitation be wiped with a strip of blotting-paper.

To keep the Plates.—I lay my plates together in pairs, film against film, with a narrow strip of blotting-paper between the edges, and wrap them up in black paper. It is best not to put more than one pair together in a packet, on account of possible damage to the film. The packets are stored in a plate cupboard or a light-tight box in a dry place.

Unpacked plates tend to become fogged sooner than those in packets. But plates which are to be used shortly after preparation may be kept without packing from eight to fourteen days in a light-tight place. But I must add a warning against tin-plate receptacles. This metal seems to cause fogging even without direct contact.

The Dry Plate.—Its colour is milky white, with a touch of green, in reflected light, and dark yellow in transmitted light, and the film less pure than it appears to be in the former case. Even after innumerable attempts I have not yet succeeded in preparing such homogeneous films as can be obtained with the silver bromide gelatin plate. With the most careful cleansing of the emulsion, and observing the greatest cleanliness throughout, it still shows differences in intensity, dark spots, and sometimes holes like pin-pricks. If it is compared in transmitted light with an ordinary dry plate, it gives very little impression of trustworthiness, on account of its transparency and the thinness (0·003—0·004 m.m.) of its film. The attempt to gauge its spectrographic value in this way would result in a very unfavourable judgment of its adaptability to exact

* *Annalen der Physik*, 1901, vol. v.

spectral uses. But experience has proved that the opposite is the case, that these film blemishes in no way spoil the purity and definition of the spectrum lines, as they only appear in the negative when the plate is too old and is already fogged.

The plate is specially sensitive towards mechanical impressions. Thus it cannot even bear dusting with a brush; the finest hair leaves traces which are obvious before developing, and more so afterwards in the negative, where they appear as fine black lines.

For the same season it requires, on cutting, very careful handling. It is best cut through the film, when narrow strips of paper, not too thin, should be laid upon the edge of the plate under the ruler which guides the diamond. One must beware that the strips of paper may leave behind spots which develop simultaneously with the picture. Therefore the strips should be so narrow that the part of the film which is to receive the spectrum may not be injured.

The Stability of the Plate.—For the first few days after preparation the plate is not very sensitive and it lacks intensity. Therefore at this time it needs unusually strong developers, solutions of a concentration which could not be used for the dry plate for fear of fogging. In this case there is no fear of displacing the film. The coating of the plate exhibits great resistance capacity towards certain chemicals. Fuming nitric acid, concentrated sulphuric, hydrochloric, and potash solution 1 : 3, &c., do not attack it. Fuming nitric acid destroys neither the latent nor the developed picture. The acid merely diminishes the intensity. This behaviour of the film is all the more remarkable in that gelatin, which is one of the constituents of the film, is easily soluble in nitric acid. We must conclude from this that the degree of solubility of the gelatin is in this case dependent on the thickness of the film.

The plate increases by keeping in sensitiveness and intensity; one to two weeks after the preparation, both give evidence of a marked increase, and there is a further increase especially exhibited in the latter. Plates one to two months old have given me the best results. In the third month there are already traces of fog. But by a large addition of potassium bromide to the developer transparent negatives can still be obtained. Plates stored in dry air have even kept faultless for nearly two years, but with these there is a noticeable decrease of sensitiveness. As the clearness of the picture in this case depends upon a further increase in the addition of potassium bromide, which lengthens the time of exposure, I cannot recommend so old a plate.

(To be continued).

CONTRIBUTIONS TO THE SCIENCE OF NITROCELLULOSE.*

By G. LUNGE and J. BEBIE.

(Continued from p. 31).

Where not otherwise stated, the appended results following refer to a mixture of three parts ether (sp. gr. 0·720) and one part alcohol (sp. gr. 0·810). But, as will be demonstrated later, the same results may also be obtained with numerous other proportions of the mixture.

For the determination of unchanged cellulose and oxycellulose *cf.* Part B.

A. *Influence of Water upon the Process of Nitration.*

The principal factors in the production of nitrocellulose are the relative proportions of nitric acid, sulphuric acid, and water; this relation determines in great degree the result of nitration. Since many of the stages of nitration of cellulose have been put to great industrial use, the necessity has arisen of knowing as nearly as possible the different mixture proportions of those three bodies in their influence upon the progress of nitration. It is naturally impossible to examine individually all the innumerable possible combinations; but it ought to be possible to gain an accurate insight into these complex relations by means of numerous systematically arranged series of experiments.

Vieille was the first to undertake a research with this intention. He started with a sulphuric acid of sp. gr. 1·832, and mixed one part of the same with different quantities respectively of a nitric acid of sp. gr. 1·316. In this manner he obtained, from twelve different proportions, nitrocelluloses containing from 132·7 to 195·9 c.c. NO. In this method of nitration there are therefore two variable quantities, nitric acid and water, and the results obtained must therefore be considered as due to the action of these two factors. We notice the same in the research carried out later by Bruley. His results afford a survey of the influence of a great number of combinations of nitric acid, sulphuric acid, and water; but, on the other hand, the absolute action of any one of these three factors is only visible in them to a limited extent. But this knowledge should be of value for further researches, and it was the object of the first part of this work to obtain it.

Next, therefore, it was necessary to determine the influence of the water upon the process of nitration in the least ambiguous manner possible, for which purpose the following method was pursued:—The nitration mixture consisted of equal parts by weight of sulphuric acid 1·83 and nitric acid 1·5 (free from lower nitrous oxides). Equal portions of this were now treated with varying quantities of water. Therefore the ratio of nitric acid to sulphuric acid was the same in all the nitration mixtures. The remaining factors, *e.g.*, temperature, time of nitration, relation of the cellulose to the amount of nitric acid contained in the mixture, were kept as constant as possible; hence the water was the only variable, and the results are entirely traceable to the action of this one factor.

The temperature was that of the surroundings, *i.e.*, 16—18° C.; the time of nitration lasted twenty-four hours. The cellulose material used was "chemically pure dressing wadding." This was boiled with dilute soda solution, well washed, and finally treated with alcohol and ether; then dried at 100° before nitration, and cooled down in the desiccator. The nitration was generally conducted in wide-necked, well-stoppered glass cylinders, but nitrations at raised temperatures in the apparatus described by Lunge and Weintraub.

After twenty-four hours the nitration mixture was poured off, the nitration product pressed upon porous porcelain to free it from most of the adhering acid, and then placed in small portions in much cold water, afterwards laid upon a porous plate, treated for some time with cold water, and finally washed with hot water as often as possible for two days.

The examination of the products obtained comprised the percentage of nitrogen, solubility in ether-alcohol, and behaviour towards polarised light. Besides this, we give the corresponding gain of nitrocellulose in 100 parts of pure cellulose used.

The accompanying table contains the results of this first series of experiments, and the analyses of the corresponding nitration mixture. These were conducted according to the commonly used methods. One test gave the total acid by titration, the other the sulphuric acid by evaporating off the nitric acid on the water-bath; the percentage of nitric acid was obtained by difference.

It may be here once for all mentioned that the numbers quoted in this work have been obtained in each case from at least two experiments agreeing well with each other.

The nitration products obtained do not, as a rule, represent individual compounds, but mixtures of different nitrocelluloses. The property of partial solubility of the products in ether-alcohol points with certainty to this fact; this was therefore used to effect a partial separation of the nitration products. Certainly the soluble portion, as also the insoluble, may again consist of a mixture of different

* *Zeitschrift fur Angewandte Chemie*, 1901, Heft 20.

Expt.	C.c. NO per 1 grm.	Per cent N.	Solubility in ether-alcohol (3 : 1).	Gain.	Nitration mixture. H_2SO_4.	HNO_3.	H_2O.
1.	217·73	13·65	1·50	177·5	45·31	49·07	5·62
2.	210·68	13·21	5·40	176·2	42·61	46·01	11·38
3.	203·49	12·76	22·00	—	41·03	44·45	14·52
4.	200·58	12·58	60·00	167·0	40·66	43·85	15·49
5.	196·35	12·31	99·14	159·0	40·14	43·25	16·61
6.	192·15	12·05	99·84	153·0	39·45	42·73	17·82
7.	184·78	11·59	100·02	156·5	38·95	42·15	18·90
8.	174·29	10·93	99·82	144·2	38·43	41·31	20·26
9.	155·73	9·76	74·22	146	37·20	40·30	22·50
10.	148·51	9·31	1·15	138·9	36·72	39·78	23·50
11.	133·94	8·40	0·61	131·2	35·87	38·83	25·30
12.	103·69	6·50	1·73	—	34·41	37·17	28·42

nitrocelluloses; but it often happened that—judging by the proportion of nitrogen—one or both of the components were single bodies. In the case of those products which contained only a small percentage of either soluble or insoluble components, it was necessary to dispense with a separate examination of both portions on account of lack of material, and only that portion was examined which contained the predominating amount; the percentage of nitrogen contained in the other portion being determined by calculation.

If, for example, the percentage of nitrogen of the insoluble portion has been determined, and we put—

a = c.c. NO per 1 grm. mixture;
b = c.c. NO per 1 grm. insoluble portion;
c = percentage solubility in ether-alcohol;
d = percentage N of the soluble portion;

then we have—

$$d = \frac{100\,(a-b)+b\,.\,c}{c}.$$

If, however, the quantity d has been already determined, we find the quantity b from—

$$b = \frac{100\,a-d\,.\,c}{100-c}.$$

But one must pay attention to the fact that the solubility determination is not very exact, especially in cases where there is only a small proportion of soluble constituents, and that, therefore, this indirect nitrogen determination cannot claim the same accuracy as the direct.

Experiment 1 yielded a product with a remarkably high percentage of nitrogen. Although the nitration mixture was not very concentrated, containing 5·6 per cent water, yet we surpassed the nitrogen content of 214 c.c., designated by Vieille as the maximum. In Section C, "The Highest Degree of Nitration attainable by means of Mixtures of Nitric Acid and Sulphuric Acid," this result is explained. The percentage of nitrogen in the product extracted with ether-alcohol was but little higher, viz., 218·00, and that of the soluble portion accounted for 200·00 c.c. NO.

The result of increasing the proportion of water is at first—up to about 11 per cent—only a slight diminution in the contained nitrogen. From the graphical representation of the results, the gradually increasing influence of the contained water is clearly visible.

The insoluble portion of the product obtained in Experiment 2 shows a proportion of nitrogen near to that of hendeca-nitrocellulose, viz., 213·25 c.c.; that of the soluble part is, by calculation, 181·4 c.c.

Experiment 3 gives a product with a percentage of nitrogen agreeing with that of decanitrocellulose. But its merely partial solubility shows it to be no simple body. The soluble portion proved to be octonitrocellulose (177 c.c. NO), while the insoluble portion gave a nitrogen percentage of 211·5 c.c. (calculated 211·00). It is clearly obvious that the percentage of nitrogen alone does not suffice to identify a nitration product. Hence the properties of a nitrocellulose, whose percentage of nitrogen corresponds to a certain stage of nitration, should not—as has often happened—be ascribed to the latter without further confirmation.

The above experiments show a somewhat large difference in the degree of nitration of the two components (insoluble and soluble portion). This might be chiefly ascribed to the dilution of the nitration mixture which sets in during the course of the reaction, and which is caused partly by the abstraction of nitric acid, and partly by the development of the water of reaction. But, as is to be inferred from this series of experiments, small percentage differences in the water content produce considerably different stages of nitration, and it is therefore easy to comprehend that during nitration no single bodies arise, but mixtures of different nitrocelluloses. The greater the mass of the nitration mixture compared with that of the cellulose, the less is the absolute change in the composition of the mixture, and hence the smaller the influence of this change on the process of nitration. Thus it appears also that the ratio of the mass of the cellulose to that of the acid mixture plays a not unimportant part.

(To be continued).

THE CRYSTALLISATION OF COPPER SULPHATE.

By ARTHUR JOHN HOPKINS.

The Size of Crystals.

The work described in this paper had for its object the preparation of crystals of copper sulphate, which should be from 20 to 30 m.m. in length. The first part contains a short discussion of those general conditions which determine the size of crystals, together with a development of a method for the preparation of crystals of any desired size. The following principles guided the work:—

I. In the process of crystallising copper sulphate, at constant room temperature, the solubility is a constant, and the concentration (weight of solute in unit volume), minus this constant is the total weight of crystal deposit. Or, in other words, in the process of crystallising copper sulphate at constant room temperature, the concentration determines the weight of the crystal deposit.

II. (*a*) In a solution, supersaturated in absolute quiet, no crystals will form.

(*b*) In a solution supersaturated in absolute quiet, the number of crystal points formed by the first disturbance (if the disturbance is succeeded by quiet) is the same as the number of crystals finally formed.

(*c*) The ratio between the number of crystals formed and the weight of crystal deposit determines the size of the crystals.

III. For a given volume of solution and given size of crystals, and weight of crystal deposit, the diameter of the crystallising dish determines the space between the crystals.

The usual laboratory practice of preparing a solution of known concentration with the expectation of getting crystals of definite size is therefore misleading, as this method gives only one definite result, *i.e.*, a certain weight of crystal deposit, as is expressed by the first principle. From principle II. it is clear that the number of crystals to be formed is determined almost instantaneously, *i.e.*, that nothing in the previous history of the solution (its concentration, the size of the dish, or the rate of cooling) directly determines the number of crystals, but that as the solution cools beyond the point of saturation, a few crystal points suddenly started, whether by direction or accidentally, will slowly grow by addition from the solution, and, if given equal opportunity, will grow equally, each crystal's final weight becoming the quotient of the total weight of crystals deposited, divided by the number of points started.

Again, from the third principle, it is evidently desirable that the dish be large enough to allow the crystals full room to grow without crowding.

The experiments of the two parts of this paper number about 60. The first experiments are passed over. They proved that neither concentration alone, nor the relation of the size of the dish to the volume of the solution, nor the rapidity of cooling determines the size of the crystals. These facts were all proved later by two experiments, as follows:—First, bring a solution of definite volume and concentration to supersaturation in absolute quiet, and then, after disturbing, note the size of crystals formed. Second, after warming the crystals and the solution obtained as described, repeat the first experiment, when crystals of an entirely different size will probably be deposited. A single such experiment shows that the slightest accident, after saturation, may determine the size of crystals.

In all of this work, dust was excluded as rigorously as possible by careful filtering of solutions and scrupulous cleaning of crystallising and other dishes. In order to prevent carbonate from forming and acting as centres of crystallisation, recently boiled water was used at first, then water known to be free from carbonic acid, but finally it was found necessary (in continued crystallisations of the same solution), to add about 5 c.c. of normal sulphuric acid to every 100 c.c. of solution. Uniformity in measuring (without danger of error due to contraction on cooling to indefinite degrees), was approximated by concentrating the filtered and perfectly clear solution in a marked beaker to a volume smaller than that desired, pouring quickly into a hot measuring cylinder, transferring the last drops by aid of a little boiling water, filling the cylinder to the desired volume with boiling water, and pouring the solution quickly into a clean crystallising dish, which was immediately covered. All of these experiments were conducted in a room held at constant temperature by a heat regulator, and a watch was kept on the indications of a maximum and minimum thermometer. A variation of 2° was unusual, and occurred only during the night.

Experiments showed that solutions of convenient concentration and volume were obtained, when 171 grms. of clean copper sulphate crystals were dissolved in water and 15 c.c. of normal sulphuric acid were added, and the whole was concentrated to less than 340 c.c., and diluted to exactly that volume with boiling water, the volume being read when the solution was as near as possible at boiling temperature. All the solutions were started in this way, and all solutions, not of the same volume, were of this concentration. The size of the crystals decided upon as desirable for quantitative work was a length varying from 20 to 30 m.m. The ratio of the volume of solution to the horizontal surface of the containing crystallising dish is identical with the depth of solution, and so for each volume a dish was selected which would give a constant depth. A depth of about 6·3 m.m. was found to give ample space between crystals 20 to 30 m.m. long, formed from a solution of the strength indicated; and in so shallow a solution there is the added advantage that the crystals, when first formed on the surface, fall to the bottom directly without slant. The diameter of the dish, which will hold 340 c.c. at a depth of 6·3 m.m., is 26 c.m., and, in general, the diameter for this depth is the square root of twice the contained volume.

From the previous discussion it will be seen that with a given volume and concentration, and with the size of the dish determined, the size of the crystals will depend upon the number of crystal points first started in the solution as it cools beyond the point of saturation, and that the number of these points depends upon the conditions which obtain in the crystallising dish during the time of supersaturation, and only then. Of course one can escape the uncertainty of accident by providing in such a solution a sufficient number of minute, clean crystals to supply nuclei for crystallisation, but these should be so small as not materially to increase the concentration. A difficulty would arise in this method of procedure in that the temperature would have to be chosen so low that the little crystals would not dissolve in the hot solution before growth began, and also so high that the cold crystals would not locally chill the surface of the solution below the saturation-point, and thus start crystallisation in a fine powder throughout the whole mass. For the volume and concentration above indicated, about fifty such points would be necessary to give crystals of 30 m.m. in length.

The method used in this work for starting the proper number of crystal points is one which, with a little practice on the part of the experimenter, works satisfactorily—how much so will be seen from the second part of this paper. When the hot measured solution is poured into the crystallising dish, the latter is carefully covered to prevent further concentration, dust, or surface chilling, and is allowed from eight to ten minutes to cool, when a slight blast of air (the air being filtered through cotton), under pressure equivalent to 12 m.m. of mercury, is blown upon the surface, and the latter is watched closely for the first minute crystals which (formed before the colder blast), float out upon the surface. When the proper number of these crystals for the volume and concentration are not only formed but persist in the hot solution, the blast is quickly removed, and the crystals are allowed to grow while the dish is covered and left undisturbed at constant temperature, usually over night. As the number of crystals always bears the same relation to the surface exposed, one watches not for a certain number of crystals but rather for a certain spacing, constant for each experiment, which it is easy to approximate each time.

Successive Crystallisations.

In the experiments mentioned above, 171 grms. of clean copper sulphate crystals were dissolved in acidified water, and concentrated to 340 c.c. On crystallisation at 23° C., 275 c.c. of mother-liquor and 78 grms. of crystals were obtained. It was desired to evaporate further the 275 c.c. of concentrated solution to the same strength as the 340 c.c. of the original solution—a concentration which will always give the ratio of 78 grms. of crystals to 275 c.c. of mother-liquor. It was calculated* that to this end any saturated solution of copper sulphate must be evaporated to 67·1 per cent of its volume, and that this will then give a mother-liquor equal to 54·3 per cent, and a crystal weight equal to 15·4 per cent of the same volume.

Based upon this calculation, a model has been constructed which is found in Table I., below. According to this table, each mother-liquor is to be concentrated to 67·1 per cent of its volume, and from it is to be obtained a weight of crystals, and a volume of new mother-liquor in the ratio of 28+ grms. to 100 c.c. Table II. contains the results of the first attempt to follow this model. By comparing these tables, it will be seen that the point of concentration indicated in the second column of Table I. was not reached exactly in any case, but the important column VI. of Table II. shows that the size of crystals has fallen each time within the desired limits of from 20 to 30 m.m. in length.

It should be said concerning the figures in columns I. to IV. that it is very difficult to measure quickly solutions which are held as closely as possible to the boiling temperature, and that an approximation to the model was all that was necessary, since large variations do not appreciably affect the results in column VI., which contains the results especially sought.

When the solution gets as small as 58 c.c., the nuclei may be supplied by introducing minute crystals—as only ten are needed in this case—but these crystals must first

* The calculation is as follows:—275 : 78 = 100 : 28·3. Solubility at 25° = 21·7 grms. $CuSO_4$, sp. gr. of solution being 1·21 + ; 21·7 grms. $CuSO_4$ = 38·8 grms. $CuSO_4,5H_2O$. Required, 0·338 V = 0·393 V = 0·283 V, or mother-liquor, V = 54·3 per cent V. Then the original solution at point of saturation at 23° must have measured 275 ÷ 0·543 = 506·4 c.c., 340 ÷ 506·4 = 67·1 per cent. evaporating ratio; 0·283 × 0·543 = 15·4 per cent, ratio of crystal weight to saturated solution.

TABLE I.—*Model.*

Process number.	I. Solution saturated at 23°. Each volume = 1·3 per cent of preceding.	II. Solution evaporated to 67·1 per cent of volume in I.	III. Weight of crystals = 15·4 per cent of volume in I.	IV. Ratio of weight of crystals to volume in I.	V. Diameter of crystallising dish to give solution in II. a depth of 6+ m.m. $D = \sqrt{2}V$.	VI. Size of crystals.
	c.c.	c.c.				
1.	[506·4 calculated]	340			$\sqrt{680} = 26$	
	275		78	0·283		
2.	275	184			$\sqrt{369} = 19$	
	149		42	0·282		
3.	149	100			$\sqrt{200} = 14$	
	81		23	0·284		
4.	81	54			$\sqrt{109} = 10·5$	
	44		12·5	0·284		

TABLE II.

	I.	II.	III.	IV.	V.	VI.
1.	*x*	340			25	20
	275		78	0·283		
2.	275	190			20	20
	157		39	0·248		
3.	157	105			13·5	26
	85		25	0·294		
4.	85	58			9·6	26
	50		12+	0·24		

be washed with hot water, and must then be large enough to exist in the hot solution. In larger solutions the method described is better.

Should one desire to form crystals of a different size, a little practice would be necessary to determine the proper conditions of spacing for that size, and the formula for the size of the crystallising dish would be somewhat changed. It would then be possible to prepare crystals of any desired size not only from the original solution but from all the successive mother-liquors.—*American Chemical Journal*, xxv., No. 5.

ON THE METEORIC STONES WHICH FELL NEAR ZOMBA, BRITISH CENTRAL AFRICA, ON JANUARY 25TH, 1899. WITH NOTES ON THE CHEMICAL ANALYSIS OF SUCH BODIES.*

By L. FLETCHER, M.A., F.G.S.,
Keeper of Minerals in the British Museum.

(Continued from p. 35).

Examination of the Blank Sodic Solution.

13. The amount of the alumina extracted by the sodic solution being appreciable though small, and the amount of sodic solution used being large, it was desirable to make similar experiments on the sodic solution itself. Taking the same amount of sodic solution (20 grms. of crystallised sodium carbonate and 2½ grms. of caustic soda), as was used in the last analysis, the following numbers were obtained:—

SiO_2 0·0049.
Fe_2O_3,Al_2O_3,SiO_2 0·0009 (the alumina and silica being probably inappreciable).
CaO 0·0005.
CaO 0·0019, due to action on the porcelain dish.
$Mg_2P_2O_7$ nil.

* From the *Mineralogical Magazine*, vol. xiii., No. 59, 1901.

Undecomposed Material: Specific Gravity.

14. The material left undecomposed by the acid and sodic solutions was white in colour, but there was admixed with it a little black material of higher specific gravity than that of the silicate; the black material was found to be chromite. The specific gravity of the admixture was determined from 1·2831 grms. of the material by means of a 3 c.c. pycnometer. The usual corrections for the temperature of the water and for the displaced air being made, it was found that the weight of the material which occupies a c.c. at 17° C. is 3·171 grms.

Undecomposed Material: Chemical Analysis.

15. 0·8981 grm. of the undecomposed material was fused with mixed potassium and sodium carbonates. There was a perceptible action on the platinum crucible involving the eventual separation of a little platinum from the magnesium pyrophosphate, but otherwise not interfering with the analysis. The chromite was partially decomposed, and the chromium which passed into solution manifested itself by the green colour of the oxides after the iron had been removed from the ignited precipitate by the Deville-Cooke method; the oxides of iron, aluminium, and chromium had been twice precipitated together in dilute solution by the sodium acetate method, and finally with ammonia; they were thus free from magnesium.

The following numbers were obtained:—

SiO_2 + chromite 0·5056.
Chromite, after treatment with HF and H_2SO_4, 0·0027.
$Fe_2O_3,Cr_2O_3,Al_2O_3,SiO_2$ 0·1545; of this 0·1201 yielded Cr_2O_3,Al_2O_3,SiO_2 0·0393, which itself on being analysed gave Cr_2O_3 0·0054, Al_2O_3 0·0314, SiO_2 0·0006, the loss being probably Al_2O_3.
MnS 0·0042.
CaO 0·0369 (a double precipitation with ammonium oxalate).
$Mg_2P_2O_7$ 0·5384.

16. *Alkalis.* — 0·4994 grm. of the undecomposed material, analysed by the Lawrence Smith method, gave:—Sodium and potassium chlorides 0·0183; K_2PtCl_6 (free from filter) 0·0079; adherent to filter and ignited 0·0025. During the operation the chromite was, partially at least, converted into chromate, and Cr_2O_3 0·0018 was separated from the alkaline solution before the mixed chlorides could be weighed.

Undecomposed Material: Action of Hydrochloric Acid and Sodic Solution.

17. It is well known that the residue from the treatment with hydrochloric acid and sodic solution is far from insensible to the action of those reagents; it became desirable to ascertain the amount of this action under similar circumstances to those of the analyses of the unattracted material itself.

1·10388 grms. of the undecomposed material were therefore treated in the same way as the unattracted material. The following numbers were obtained:—

a. Residual material.—Part washed from filter, 0·8807; part adherent to filter and ignited, 0·0363.

b. The acid solution yielded:—
FeO_3,Al_2O_3,SiO_2 0·0150; of this 0·0080 gave Al_2O_3 0·0005, and SiO_2 nil.
SiO_2 0·0022 was obtained from the solution, and is a measure of the action on the vessels.
CaO 0·0076.
After decomposition of the ammonium chloride by nitric acid, SiO_2 0·0033 and Fe_2O_3,Al_2O_3 0·0008 were separated from the solution, and were due to the action of the nitric acid on the porcelain dish.
$Mg_2P_2O_7$ 0·0649.

c. The sodic solution yielded:—
SiO_2, with trace of undecomposed material, 0·0763.

After treatment with HF and H_2SO_4 and subseqnent ignition, 0·0014.

Fe_2O_3,Al_2O_3,SiO_2 0·0071; of this 0·0060 gave Al_2O_3,SiO_2 0·0052, and the latter when analysed gave Al_2O_3 0·0048 and SiO_2 nil.

CaO 0·0028.

(Further CaO 0·0016, due to action of nitric acid on the porcelain dish).

$Mg_2P_2O_7$ nil.

Undecomposed Material: Effect of Ignition.

18. As the undecomposed material contains a considerable proportion of ferrous oxide, it was probable that ignition would appreciably increase its weight. It is necessary to determine the amount of this action, for that part of the silicate which is adherent to the filter cannot be weighed until after ignition.

0·0332 grm. of the undecomposed material, after ignition with the gas blowpipe, became 0·0331; there was thus no appreciable change of weight, the increase of weight by oxidation being neutralised by loss due to volatilisation.

Undecomposed Material: Effect of Hydrofluoric and Sulphuric Acids followed by Ignition.

19. Similarly, it is necessary to determine the effect of hydrofluoric and sulphuric acids, followed by ignition, in order to determine for each case the amount of the finely divided silicate which has passed through the pores of the filter and is admixed with the silica. It was found that 0·0696 grm. of the undecomposed material gave after this treatment a residue which weighed 0·0572.

Action of Nitric Acid on the Porcelain.

20. For the precipitation of the small amount of calcium it is necessary to add to the solution enough ammonium oxalate to convert not merely the calcium itself, but also the magnesium, into oxalate, otherwise part of the calcium may remain in solution. The large amount of ammoniacal salt thus introduced has to be removed before the precipitation of the magnesium: if this is effected by evaporation and ignition, there is great danger of loss through spurting; if it is effected by evaporation with strong nitric nitric acid, there is an appreciable action on the porcelain dish and the magnesium precipitate is not quite pure. The amount of action depends on the duration of the evaporation with nitric acid and on the amount of the latter; it will thus vary in different experiments. To gain some idea of the amount of the action, the silica and calcium thus brought into solution were on several occasions determined and have been recorded above:—

SiO_2 0·0061 (§ 11), 0·0067 (§ 12).

CaO 0·0036 (§ 4), 0·0040 (§ 9), 0·0020 (§ 10), 0·0013 (§ 11), 0·0022 (§ 11), 0·0012 (§ 12).

The mean of the numbers for the CaO is 0·0024; the weight of the corresponding $Ca_2P_2O_7$ would be 0·0054; this amount may therefore be properly subtracted from the determined weight of the $Mg_2P_2O_7$ when the amount of nitric acid used has been about the average.

(To be continued).

THE RATE OF NITRIFICATION OF SOME FERTILISERS.*

By W. A. WITHERS and G. S. FRAPS.

The value of any fertiliser depends on its availability to the plant; that is, the readiness with which it can be absorbed directly by the plant, or converted into forms which can be assimilated. Nitrogen can be assimilated by plants directly in four forms, viz., (1) free nitrogen, (2) as certain organic compounds, (3) as ammonium salts, (4) as nitrates.

Free nitrogen can be assimilated from the air by a class of plants with the aid of organisms living in nodules on their roots. This method of assimilation is confined to the leguminosæ, which includes clover, peas, beans, the peanut, vetch, &c.

Some organic compounds, such as urea, glycocoll, leucin, tyrosin, asparagin, and acetamide, may be taken up directly by plants, and serve to nourish them. All of these compounds may occur in the soil. Urea is found in urine, asparagin in plants, and asparagin and tyrosin are often produced by the decay of animal or vegetable matter in the soil. All nitrogenous organic compounds applied to the soil change to nitrates with greater or less rapidity, and in this form are readily taken up by the plant.

Ammonium salts also can be assimilated by plants. German millet, golden millet, water-melons, corn, common sorrel, and other plants seem to be able to assimilate ammonium salts directly. Ammonium salts also are converted to nitrates when placed in the soil.

While some plants can assimilate free nitrogen, others organic compounds, and still others nitrogen in the form of ammonia; nitrates appear to be the form in which nitrogen is taken up with the greatest readiness by most plants. It is also the form which all nitrogen compounds finally assume when placed in the soil.

When combined nitrogen, in whatever form of combination, is placed in the soil, it is converted into ammonium salts, nitrites, and finally nitrates, with greater or less speed, depending on the form of combination, the temperature, condition of the soil, &c., provided certain living organisms are present (and they usually are). If in any given soil, we determine the relative rate with which nitrogenous fertilisers which cannot be utilised directly by the plant, are converted into nitrates, it should throw some light upon the relative values to plants of those particular fertilisers.

This is the object of the work which will be described in the following pages.

Historical.

Müntz and Girard (*Central-Blatt Agr. Chem.*, 1891, xx., 656, Abs.) have determined the relative rate of nitrification of some fertilisers. A small quantity of the fertiliser was intimately mixed with natural soil, and kept at the temperature of 15—25° C., properly moistened, and at the end of a given period leached with water, and the nitrate determined in the extract. The nitrate existing in the soil at the beginning of the experiment was previously determined. The time was thirty, thirty-two, and thirty-nine days for different sets. The nitrogen converted into nitrates, and the nitrogen recovered from the soil by horse-tooth corn in two years, is shown in the following table:—

	Nitrified in thirty days. Per cent.	Recovered by corn. Per cent.
Ammonium sulphate	75·0	76·7
Dried blood	72·4	55·0
Roasted horn, fine	71·0	60·1
Flesh meal	70·4	—
Horn trimmings, fine	55·5	53·3
Poudrette, rather coarse	18·1	14·9
Roasted leather, fine	11·6	38·3
Leather chips, raw	0·4	—

In another series, the order of nitrification was as follows:—Bat guano, dried grasshoppers, dried cockchafers, flesh meal, dried blood (the substance nitrified to the greatest extent being given first). There is very little difference between the three substances named last. The nature of the soil has a great influence on the change. Nitrification was most active in a light soil from Joinville (used in the experiment referred to above), then in a garden soil, then in a chalky soil, then in a marled moor soil. Very little nitrification occurred in a very calcareous clay, except with cow manure, and yellow lupins, which loosened their texture; and none in an acid moor soil with the same two exceptions.

* Contribution from the North Carolina Agricultural Experiment Station. From the *Journal of the American Chemical Society*, xxiii., No. 5.

P. Bonâme (*Expt. Station Record*, ix., 732, Abs.) determined the nitrates in the drainage water from a sandy soil deficient in lime to which fertilisers had been added. The order of nitrification at the end of the first month was found to be—fish guano (most rapid), blood, fertiliser, oil cake, and ammonium sulphate. When calcium carbonate was added, nitrification took place more rapidly, but the order was still dried blood, oil cake, ammonium sulphate (see Table I.).

TABLE I.

Nitrate Nitrogen in 100 grms. Soil (in m.grms.).

	One month.	Two months.	Three months.
Soil	4·2	5·0	5·0
Soil and ammonium sulphate.	22	29	35
Soil and dried blood	66	74	85
Soil and oil cake	59	82	95
Soil and fish guano	74	110	113
Soil and calcium carbonate ..	6·2	7·3	6·0
Soil, calcium carbonate, and ammonium sulphate	75	133	186
Soil, calcium carbonate, and dried blood	123	151	159
Soil, calcium carbonate, and oil cake..	97	139	137

It will be noted that where calcium carbonate was not used, nitrates were formed more slowly through the entire period from ammonium sulphate than from the organic substances used. When calcium carbonate was added, the quantity of nitrates produced for the first and second months from ammonium sulphate was smaller than from the organic substances. At the end of the third month, a larger quantity of nitrates was formed from ammonium sulphate than from organic materials.

Experimental.

Effect of Dilution of Soil.—The effect of ratio of soil to fertiliser was studied in some preliminary experiments. 3000 grms. of a sandy soil from a pasture, which had been sifted through a 6-mesh sieve, was mixed well with the quantity of dried blood containing 1·0, 0·5, 0·25 grm. nitrogen, and the mixtures placed in a dark closet for fourteen days. They were watered at suitable intervals, endeavouring to maintain the original 10 per cent of water. The temperature was about 27° C. The nitrates were leached out at the end of the period, and their quantity determined by the Tiemann-Schulze method. Results are given in Table II.

TABLE II.

	Dilution.	Nitrates. Grm.	Nitrified. Per cent.
Soil	—	0·0963	—
Soil and 1·0 grm. nitrogen	1/3000	0·4564	36·0
Soil and 0·5 grm. nitrogen	1/6000	0·3626	52·3
Soil, 0·5 grm. nitrogen, and 1·785 grm. calcium carbonate	—	0·5043	81·6
Soil and 0·25 grm. nitrogen	1/12000	0·2354	55·6

The rapidity of the nitrification is influenced very decidedly by the dilution, and increased by calcium carbonate from 100 to 156. Thirty pounds of nitrogen per acre is a liberal application for a fertiliser. Assuming that the mean weight of a cubic foot of soil is 80 pounds, and that the soil is cultivated to the depth of 6 inches, then the dilution of the nitrogen applied as a fertiliser is 1/57000, which is much greater than in any of the above cases. But it must be remembered that a fertiliser is never mixed intimately with the soil, and is often in lumps, so that the actual soil surface in contact with the fertiliser is probably much less than 1/12000. This would be particularly true with materials like dried blood, which are insoluble in water. Soluble fertilisers, like ammonium sulphate, would diffuse until they become fixed, or the soil water becomes of a uniform composition; the diffusion of salts in a soil must be a very slow process.

(To be continued).

CORRESPONDENCE.

THE DIRECT ESTIMATION OF CARBON IN METALS.

To the Editor of the Chemical News.

SIR,—There should be no difficulty in getting red-lead free from carbonates. A red-lead which gives 1 per cent of carbon, equal to about 3·6 per cent of carbonic acid, or, in other words, consisting of white-lead to the extent of one-third, is well described as of the "*worser*" (with the accent on the last syllable) kinds. Possibly had your correspondent shown the sample to his paint friends they would have told him that the sample did not consist of red-lead at all, but was a barytes dyed with a coal-tar colour, and that his 1 per cent carbon came mostly from the latter. The market is flooded with such rubbish; some firms getting weekly bulky consignments of barytes from the Continent for this and similar purposes (*vide* Custom House returns). *Orange* lead, made by furnacing *white-lead*, must not be confounded with *red-lead* made by furnacing *litharge*, although any one outside the paint trade might not be able to differentiate by mere sight between them any more than he would between the sophisticated article just referred to and the genuine red-lead. The orange lead, however, effervesces when treated with dilute acetic acid. *Red-lead should not.* Orange lead at the most contains not more than 6 per cent of undecomposed carbonate. It is therefore ridiculous to say that there is any red-lead whatever on the market which has carbonate to the extend of one-third. But why use red-lead at all? Commercial nitrate of lead and "bichrome" are almost chemically pure, and may be had quite cheap from any drysalter. Why therefore cannot the steel-works chemist make his own chromate of lead by mutual decomposition of the above in the proportion of two equivalents of nitrate of lead 660 parts, to one equivalent of bichrome 295 parts, wash thoroughly with distilled water, and dry completely? He would thus have a genuine chrome-yellow—far superior to anything he would be likely to meet with in commerce or get from "pure" chemical dealers.

His "blanks" would thus be reduced to a minimum. His reagents would be, like Cæsar's wife, above suspicion. Many dealers in "pure" chemicals free from so-and-so get them from paint, &c., manufacturers who know nothing about them and care less. They are supposed to be makers, but sell them as they buy them. How any chemist worthy of the name can be satisfied with mere "blank" determinations as the only test of their reagents passes my comprehension. Do they not make a qualitative examination of them at the least, or make a determination on a sample containing a known percentage of carbon? The reagent has a certain work to do besides yielding a greater or less result in a blank experiment. The following hints may be of use in testing:—Genuine red-lead gives no effervescence with dilute acetic acid, cedes nothing to ammoniated alcohol, and is completely soluble in dilute nitric acid plus oxalic acid. Genuine chromate of lead cedes nothing to ammoniated alcohol, dissolves instantaneously in a large excess of potash, and is re-precipitated by acetic acid.

Nitric acid, concentrated or dilute, in the hot or in the cold, has no action whatever on genuine peroxide of lead, but dissolves it instantly on the addition of oxalic acid and water if the concentrated acid has been used. The writer would not put himself to the trouble of performing a blank experiment on any of these three substances which did not fulfil the requirements of these and other tests, and would reject them even if the blank were completely negative, as not being what they were represented to be, and therefore presumably unfit for the purpose for which they were intended.—I am, &c.,

J. G. McINTOSH.

London, E.

Dr. JERWITZ'S FAT-EXTRACTION APPARATUS.

To the Editor of the Chemical News.

Sir,—An illustrated description of the above apparatus was recently given in the Chemical News (vol. lxxxiii., p. 229). As, however, its somewhat complicated and fragile appearance may possibly operate against its adoption by technical chemists and analysts engaged in the estimation of fats, it may interest your readers to know that Dr. Jerwitz's apparatus has been exclusively used in this laboratory during the past twelve months with the most satisfactory results.

The extractor and condenser being in one piece, there are no troublesome cork or mercury joints to attend to, and the extractor being joined to one side of the condenser, the sample can be placed in position ready for extraction, by simply removing and replacing a ground glass stopper, the apparatus itself, once fixed in position on a stand, or against a wall, never requiring to be disturbed. Used in conjunction with a capacious water bath, the temperature of which is controlled by a thermo-regulator, and with a constant supply of cold water for condensing, the apparatus is perfectly automatic in its action, and requires absolutely no attention during the extraction. It is so simple and reliable in operation that it only requires to be known to be widely adopted.—I am, &c.,

William W. Mellon.

Laboratory,
81, Rogerson's Quay, Dublin.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 1, July 1, 1901.

Chemical Equilibrium. Phosphoric Acid and the Chlorides of the Alkaline Earths.—M. Berthelot.—From the observations and experiments described in this paper, it may be apparently shown that the relation between a molecule of phosphoric acid in combination and an equivalent number of alkaline earth bases, which combine to saturate this molecule in the phosphate precipitates, vary from two to four equivalents, according to the nature and the relative proportions between the bodies placed in contact, the free or combined acids or bases, alkaline earth chlorides, &c. These variations are always a function of the time elapsing since the beginning of the reaction.

New Treatment of Niobite. Preparation and Properties of Fused Niobium.—Henri Moissan.—By means of the electric furnace it is easy to obtain a mixture of niobium and tantalum. From this mixture, by applying Marignac's method, the niobium and tantalum can be separated and obtained in the form of oxide. Niobic acid, which was absolutely non-reducible by means of carbon at the highest temperature of an ordinary furnace, can be reduced in the electric furnace, and gives a compact mass of the metal, which is very hard and contains a very small quantity of combined carbon. This mass is solid at the fusing-point of platinum; it is only attacked by acids with great difficulty, and has no action on water-vapour at a red heat, but burns in oxygen with ease, producing a stable acid; it possesses at the same time very curious reducing properties. These various properties seem to separate niobium from the metals and bring it closer to the simple non-metals boron and silicon.

Acidimetry of Arsenic Acid.—A. Astruc and J. Tarbouriech.—The saturation of arsenic and phosphoric acid by the alkaline bases seems to be very similar in its action. On the contrary, it differs in several points when saturation is effected with the alkaline-earth bases; in particular, the tri-metallic salt obtained in cold dilute solution by arsenic acid in presence of the alkali and excess of a chloride of an alkaline earth. This is transformed into a di-metallic salt, from which the excess of base is saturated by the acid used for titration. This latter reaction does not take place with phosphoric acid.

A Colourless Compound of Sodium Tetrazotolylsulphite with Ethyl-β-naphthylamine and its Transformation into a Colouring-matter.—A. Seyewetz and M. Blanc.—Sodium sulphite gives, with the di- and tetrazoic derivatives, compounds in which the properties characteristic of diazoic bodies are masked—which, in fact, do not give colouring-matters with the amines and phenols. If, however, the sulphite derivative, when added to the amine or the phenol, is left exposed to light, the colouring-matter is produced. The authors investigate the mechanism of this reaction, and examine the colouring-matters produced in each case.

Action of Benzoic Aldehyde on Sodium Menthol, and New Methods of Preparation of Benzylidene Menthone.—C. Martine.—The author's experiments apparently show—(1) That sodium menthol behaves in the same manner as borneol with regard to benzoic aldehyde, and it gives with this substance benzylidene menthone; (2) the reaction takes place probably according to the equation given by Claisen; (3) the benzylidene menthone can also be obtained by treating sodium menthone with benzoic aldehyde.

Union of Camphor with β-Oxy-α-naphthoic Aldehyde.—André Helbronner.—Haller has shown that camphor is susceptible of uniting with a certain number of aromatic aldehydes to give perfectly definite crystalline compounds corresponding to the formula $C_8H_4\begin{cases}C=CH-R\\ \\ CO\end{cases}$.

It is interesting to discover that an analogous compound can be produced with β-oxy-α-naphthoic aldehyde. The author was not able to experiment with the aldehyde itself. Indeed, the sodium of sodium-camphor would give the sodium compound, on account of the hydrogen in the OH-group. However, good results were obtained by working with the ether-oxides of this aldehyde.

Action of Bromacetophenone on Sodium Acetylacetone.—Fr. March.—The author obtains a triacetone of the type $(CH_3—CO)_2=CH—CH_2—CO—CH_3$ by acting with bromacetophenone on sodium acetylacetone. The action apparently takes place according to the equation—

$$(CH_3—CO)_2=CHNa+CH_2Br—CO—C_6H_5=$$
$$=NaBr+(CH_3—CO)_2=CH—CH_2—CO—C_6H_5.$$

MISCELLANEOUS.

Pocket-Book of Electrical Engineering Formulæ.—The second edition of Geipel and Kilgour's "Pocket-Book of Electrical Engineering Formulæ" is just issued by *The Electrician* Publishing Company, London, price 7s. 6d. nett. The authors, who both occupy a prominent position in the electrical industry, and are in close touch with the latest practice in all matters relating to the applications of electricity to industrial purposes, have carefully revised and added to the matter which forms the chief contents of the book. Electric Traction, the Transmission of Electric Power, and the many other subjects which, since the first publication of the Pocket-Book, have come prominently to the front, have been given special attention, with the result that the book contains over 850 pages. The use of a thin, hard paper, and a compact binding has enabled the Publisher to reduce the bulk of the work, which is, notwithstanding the mass of matter crowded between the covers, not too large for the pocket. The electrical engineer engaged in practical everyday work will find the Pocket-Book of great service.

Action of Sulphochloride of Phosphorus on the Aromatic Amines in the Presence of an Alkali.—W. Autenrieth and P. Rudolph.—The authors have attempted to react on the aromatic amines with sulphochloride of phosphorus in the presence of an alkali, and they have observed that the reaction proceeds as with the oxychloride of phosphorus. In this reaction neutral derivatives of the orthosulphophosphoric acids of the general formula $SP(NHR)_2$ are very easily obtained, and these crystallise very well. In much less quantity they obtained disubstituted sulphosphoric acids of the formula $SP(NH.R)_2OH$. These latter, which crystallise with difficulty and are not very stable, have not been examined very closely; the authors have been content to examine the principal product which is formed according to the equation—

$$SPCl_3+3C_6H_5.NH_2+3NaOH= \\ =SP(NHC_6H_5)_3+3NaCl+3H_2O.$$

The authors also describe, in the same paper, the derivatives obtained by the "sulphophosphorylation" of aniline, of *p*-toluidine, and of *p*-phenitidine.—*Berichte*, vol. xxxiii., p. 2112.

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THE CHEMICAL NEWS.

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THE NADIR OF TEMPERATURE, AND ALLIED PROBLEMS.*

1. PHYSICAL PROPERTIES OF LIQUID AND SOLID HYDROGEN. 2. SEPARATION OF FREE HYDROGEN AND OTHER GASES FROM AIR. 3. ELECTRIC RESISTANCE THERMOMETRY AT THE BOILING-POINT OF HYDROGEN. 4. EXPERIMENTS ON THE LIQUEFACTION OF HELIUM AT THE MELTING-POINT OF HYDROGEN. 5. PYROELECTRICITY, PHOSPHORESCENCE, &c.

BY JAMES DEWAR, LL.D., D.Sc., F.R.S., &c.

DETAILS are given in this paper which have led to the following results:—

The helium thermometer which records 20·5° absolute as the boiling-point of hydrogen, gives as the melting-point 16° absolute. This value does not differ greatly from the value previously deduced from the use of hydrogen gas thermometers, viz., 16·7°. The lowest temperature recorded by gas thermometry is 14·5°, but with more complete isolation and a lower pressure of exhaustion, it will be possible to reach about 13° absolute, which is the lowest temperature that can be commanded by the use of solid hydrogen. Until the experiments are repeated with a helium gas thermometer filled at different pressures, with the gas previously purified by cooling to the lowest temperature that can be reached by the use of solid hydrogen, no more accurate values can be deduced.

The latent heat of liquid hydrogen about the boiling-point as deduced from the vapour pressures and helium-thermometer temperatures, is about 200 units, and the latent heat of solid hydrogen is about 16 units.

The order of the specific heat of liquid hydrogen has been determined by observing the percentage of liquid that has to be quickly evaporated under exhaustion in order to reduce the temperature to the melting-point of hydrogen, the vacuum vessel in which the experiment is made being immersed in liquid air. It was found that in the case of hydrogen the amount that had to be evaporated was 15 per cent. This value along with the latent heat of evaporation, gives an average specific heat of the liquid between freezing- and boiling-point of about 6. When liquid nitrogen was similarly treated for comparison, the resulting specific heat of the liquid came out 0·43, or about 6 per atom. Hydrogen therefore follows the law of Dulong and Petit, and has the greatest specific heat of any known substance.

The same fine tube used in water, liquid air, and liquid hydrogen gave respectively the capillary ascents of 15·5, 2, and 5·5 divisions. The relative surface tension of water, liquid air, and liquid hydrogen are therefore in the proportion of 15·5, 2, 0·4. In other words, the surface tension of hydrogen at its boiling-point is about one-fifth that of liquid air under similar conditions. It does not exceed one thirty-fifth part the surface tension of water at the ordinary temperature.

The refractive index of liquid hydrogen determined by measuring the relative difference of focus for a parallel beam of light sent through a spherical vacuum vessel filled in succession with water, liquid oxygen, and liquid hydrogen, gave the value 1·12. The theoretical value of the liquid refractive index is 1·11 at the boiling-point of the liquid. This result is sufficient to show that hydrogen, like oxygen and nitrogen in the liquid condition, has a refractivity in accordance with theory.

Free hydrogen, helium, and neon have been separated from air by two methods. The one depends on the use of liquid hydrogen to boil the dissolved gases out of air kept at a temperature near the melting-point of nitrogen; the other on a simple arrangement for keeping the more volatile gases from getting into solution after separation by partial exhaustion. By the latter mode of working something like 1/3400oth of the volume of the air liquefied appears as uncondensed gas. The latter method is only a qualitative one for the recognition and separation of a part of the hydrogen in air. In a former paper on the "Liquefaction of Air and the Detection of Impurities" (*Chem. Soc. Proc.*, 1897), it was shown that 100 c.c. of liquid air could dissolve 20 c.c. of hydrogen at the same temperature. The crude gas separated from air by the second method gave on analysis—hydrogen 32·5 per cent, nitrogen 8 per cent, helium, neon, &c., 60 per cent. After removing the hydrogen and nitrogen the neon can be solidified by cooling in liquid hydrogen and the more volatile portions separated.

There exists in air a gaseous material that may be separated without the liquefaction of the air. For this purpose air has to be sucked through a spiral tube filled with glass-wool immersed in liquid air. After a considerable quantity of air has been passed, the spiral is exhausted at the low temperature of the liquid air-bath. The spiral tube is now removed, and allowed to heat up to the ordinary temperature, and the condensed gas taken out by the pump. After purification by spectroscopic fractionation, the gas filled into vacuum tubes gives the chief lines of xenon. The spectroscopic examination of the material will be dealt with in a separate paper by Professor Liveing and myself. A similar experiment made with liquid air kept under exhaustion, the air current allowed to circulate being under a pressure less than the saturation pressure of the liquid to prevent liquefaction, resulted in krypton being deposited along with the xenon.

A study of fifteen electric resistance thermometers as far as the boiling-point of hydrogen has been made, and the results reduced by the Callendar and Dickson methods. The following table gives the results for seven thermometers, viz., two of platinum, one of gold, silver, copper, and iron, and one of platinum-rhodium alloy. It will be noted that the lowest boiling-point for hydrogen was given by the gold thermometer. Next to it came one of the platinum thermometers, and then silver, while copper and the iron differ from the gold value by 26 and 32 degrees respectively. The gold thermometer would make the boiling-point 23·5° instead of the 20·5° given by the gas thermometer. Then the reduction of temperature under exhaustion amounts to only 1° instead of 4° as given by the gas thermometer. The extraordinary reduction in resistance of some of the metals at the boiling-point of hydrogen is very remarkable. Thus copper has only 1/105th, gold 1/30th, platinum 1/35th to 1/17th, silver 1/24th the resistance at melting ice, whereas iron is only reduced to 1/8th part of the same initial resistance. The real law correlating electric resistance and temperature within the limits we are considering is unknown, and no thermometer of this kind can be relied on for giving accurate temperatures up to and below the boiling-point of hydrogen. The curves are discussed in the paper, and I am indebted to Mr. J. H. D. Dickson and Mr. J. E. Petavel for help in this part of the work.

Helium separated from the gas of the King's Well, Bath, and purified by passing through a U-tube immersed in liquid hydrogen, was filled directly into the ordinary form of Cailletet gas receiver used with his apparatus, and subjected to a pressure of 80 atmospheres, while a portion of the narrow part of the glass tube was immersed in liquid hydrogen. On sudden expansion from this pressure to atmospheric pressure a mist from the production of some solid body was clearly visible. After several compressions and expansions, the end of the tube contained a small amount of a solid body that passed directly into gas when the liquid hydrogen was removed, and the tube kept in the vapour of hydrogen above the liquid. On

* Abstract of the Bakerian Lecture read before the Royal Society, June 13, 1901.

Electrical Resistance Thermometry at the Boiling-point of Hydrogen.

Metals.	Platinum (P_1).	Potassium (P_{27}).	Alloy platinum rhodium ($Pt\text{-}Rh_{29}$).	Gold (Au_{40}).	Silver (Ag_{18}).	Copper (Cu_{47}).	Iron (Fe_{80}).
R_I	4·2050	39·655	36·87	16·10	8·336	11·572	4·290
R_0	3·1037	28·851	31·93	11·58	5·990	8·117	2·765
Resistance at CO_2	—	19·620					
,, liq. O	0·9473	7·662	22·17	3·380	1·669	1·589	0·633
,, liq. N	—	—	—	—	—	1·149	
,, liq. O*x*	—	4·634	20·73				
,, liq. H	0·183	0 826	18·96	0·381	0·244	0·077	0·356
,, liq. H*x*	—	0·705	18·90	0·298	0·226	0·071	
α	0·003548	0·003745	0·003607	0·003903	0·003917	0·004257	0·005515
$\Omega' = -\frac{1}{\alpha}$	−281·81	−267·04	−646·37	−256·19	−255·33	−234·93	−181·31
T. observed o liq. O (°C.)	−182·5	−182·34	−182·4	−182·37	−182·41	−182·41	−182·85
δ	2·5797	2·6767	4 7447	−0·18448	0·34553	1·2676	−8·3238
Calculated temp. (°C.)—							
At CO_2	—	−81·48 −80·18					
,, liq. O	−182 505	−182·342	−282 401	−182·37	−182·41	−182·413	−182·855*
	−182 601	−181·60	−183 51	−182·4	−182·41	−183·320	−182·850†
,, liq. N	—	—	—	—	—	−194 42 −195·22	
,, liq. O*x*	—	−207·12 −206·55	−207·87 −208·99				
,, liq. H	−243 61	−237·88	−238·73	−249·37	−242·06	−223·54	−213·82*
	−243·13	−237·55	−239 75	−249·5	−242·06	−223·99	−210·29†
,, liq. H*x*	—	−238 85	−239·77	−251·23	−242·84	−223·70	— *
		−238 48	−240·78	−251·1	−242·82	−224·15	— †
Ω	−258·00	−244·50	−543·39	−257·90	−252·26	−225·62	−258·40*
	−257·28	−244·15	−530·32	−257·8	−252·25	−226 04	−246·80†
Ratio $\frac{R_0}{\text{Res. at B.P. of H.}}$	16·96	34·93	1·684	30·39	24·55	105·41	7·767

R_I, R_0, are the resistances at 100° C. and 0° C. respectively. The remaining resistances are clear from the table.

x means that the liquid is boiling under exhaustion measured by about 30 m.m. of mercury.

Ω' is the temperature, in degrees of the metal in question, at which the resistance would vanish.

Ω is the temperature Centigrade at which the resistance would vanish, either on the Callendar or on the Dickson method.

Calculated temperatures—the upper, Callendar's method; the lower by Dickson's.

Callendar's α and δ are calculated from the given values of R_I, R_0, the resistance of liquid O, and the temperature observed in liquid O.

The same data are used to calculate the Dickson formula, except in the cases of P_1, whose formula is given in the *Phil. Mag.*, June, 1898; P_7, whose formula is given in *Roy. Soc. Proc.*, vol. lxiv., p. 228; and $Pt\text{-}Rh_{29}$, Arg_{32}, and Cu_{47}, which were calculated by least squares.

* Callendar. † Dickson.

lowering the temperature of the liquid hydrogen by exhaustion to its melting-point, which is about 16° absolute, and repeating the expansions on the gas from which the solid had separated by the previous expansions at the boiling-point or 20·5°, *no mist was seen*. From this it appears the mist was caused by some other material than helium, in all probability neon, and when the latter is removed no mist is seen, when the gas is expanded from 80 to 100 atmospheres, even although the tube is surrounded with solid hydrogen. From experiments made on hydrogen that had been similarly purified like the helium and used in the same apparatus, it appears a mist can be seen in hydrogen (under the same conditions of expansion as applied to the helium sample of gas), when the initial temperature of the expanding gas was twice the critical temperature, but it was not visible when the initial temperature was about two and a-half times the critical temperature. This experience applied to interpret the helium experiments, would make the critical temperature of the gas under 9° absolute.

Olszewski in his experiments expanded helium from about seven times the critical temperature under a pressure of 125 atmospheres. If the temperature is calculated from the adiabatic expansion starting at 21° absolute, an effective expansion of only 20 to 1 would reach 6·3°, and 10 to 1 of 8·3°. It is now safe to say, helium has been really cooled to 9° or 10° absolute without any appearance of liquefaction. There is one point, however, that must be considered, and that is the small refractivity of helium as compared to hydrogen, which, as Lord Rayleigh has shown, is not more than one-fourth the latter gas. Now as the liquid refractivities are substantially in the same ratio as the gaseous refractivities in the case of hydrogen and oxygen, and the refractive index of liquid hydrogen is about 1·12, then the value for liquid helium should be about 1·03, both taken at their respective boiling-points. In other words, liquid helium at its boiling-point would have a refractive index of about the same value as liquid hydrogen at its critical point, and as a consequence, small drops of liquid helium forming in the gas near its critical point would be far more difficult to see than in the case of hydrogen similarly situated.

The hope of being able to liquefy helium, which would appear to have a boiling-point of about 5° absolute, or one-fourth that of liquid hydrogen, is dependent on subjecting helium to the same process that succeeds with hydrogen; only instead of using liquid air under exhaustion as the primary cooling agent, liquid hydrogen under exhaustion must be employed, and the resulting liquid collected in vacuum vessels surrounded with liquid hydrogen. The following table embodies the results of experience and theory:—

	Initial temperature.	Critical temperature.	Boiling-points.
Liquid helium ?.. ..	5°?	2°?	1°?
Solid hydrogen	15	6	4
Liquid ,, ...	20	8	5 (He?)
Exhausted liquid air..	75	30	20 (H)
52°C.	325	130	86 (Air)
Low red heat	760	304	195 (CO_2)

The first column gives the initial temperature before continuous expansion through a regenerator, the second the critical point of the gas that can be liquefied under such conditions, and the third the boiling-point of the resulting liquid. It will be seen that by the use of liquid or solid hydrogen as a cooling agent we ought to be able to liquefy a body having a critical point of about 6° to 8° absolute, and boiling-point of about 4° or 5° absolute. Then, if liquid helium could be produced with the probable boiling-point of 5° absolute this substance would not enable us to reach the zero of temperature; another gas must be found that is as much more volatile than helium as it is than hydrogen in order to reach within 1° of the zero of temperature. If the helium group comprises a substance having the atomic weight 2, or half that of helium, such a gas would bring us nearer the desired goal. In the meantime the production of liquid helium is a difficult and expensive enough problem to occupy the scientific world for many a day.

A number of miscellaneous observations have been made in the course of this inquiry, among which the following may be mentioned. Thus the great increase of phosphorescence in the case of organic bodies cooled to the boiling-point of hydrogen under light stimulation is very marked, when compared with the same effects brought about by the use of liquid air. A body like sulphide of zinc cooled to 21° absolute, and exposed to light, shows brilliant phosphorescence on the temperature being allowed to rise. Bodies like radium that exhibit self-luminosity in the dark, cooled in liquid hydrogen maintain their luminosity unimpaired. Photographic action is still active although it is reduced to about half the intensity it bears at the temperature of liquid air. Some crystals when placed in liquid hydrogen become for a time self luminous, on account of the high electric stimulation brought about by the cooling causing actual electric discharges between the crystal molecules. This is very marked with some platino-cyanides and nitrate of uranium. Even cooling such crystals to the temperature of liquid air is sufficient to develop marked electrical and luminous effects.

Considering that both liquid hydrogen and air are highly insulating liquids, the fact of electric discharges taking place under such conditions proves that the electric potential generated by the cooling must be very high. When the cooled crystal is taken out of either liquid and allowed to increase in temperature, the luminosity and electric discharges take place again during the return to the normal temperature. A crystal of nitrate of uranium gets so highly charged electrically that, although its density is 2·8, and that of liquid air about 1, it refuses to sink, sticking to the side of the vacuum vessel and requiring a marked pull on a silk thread, to which it is attached, to displace it. Such a crystal rapidly removes cloudiness from liquid air by attracting all the suspended particles on to its surface. The study of pyro-electricity at low temperatures will solve some very important problems.

During this inquiry I have had the hearty co-operation of Mr. Robert Lennox, to whom my thanks are due, and Mr. J. W. Heath has also given valuable assistance.

The Accumulator Industries, Limited, beg to notify that their registered offices have been transferred to the works premises at Maybury, Woking, Surrey. The London offices remain as heretofore, 14, Silver Street, Bloomsbury, W.C.

ON THE SEPARATION OF THE LEAST VOLATILE GASES OF ATMOSPHERIC AIR, AND THEIR SPECTRA.*

By G. D. LIVEING, M.A., Sc.D., F.R.S., Professor of Chemistry in the University of Cambridge, and JAMES DEWAR, M.A., LL.D., F.R.S., Fullerian Professor of Chemistry, Royal Institution, London.

(Concluded from p. 38).

THE pressure p, of a gas G, above the same material in the liquid state, at temperature T, is given approximately by the formula—

$$\log p = A - \frac{B}{T},$$

where A and B are constants for the same material. For some other gas G' the formula will be—

$$\log p_1 = A_1 - \frac{B_1}{T},$$

and—

$$\log \frac{p}{p_1} = A - A_1 + \frac{B_1 - B}{T}.$$

Now for argon, krypton, and xenon respectively the values of A are 6·782, 6·972, and 6·963, and those of B are 339, 496·3, and 669·2; so that for these substances, and many others, $A - A_1$ is always a small quantity, while—

$$\frac{B_1 - B}{T}$$

is considerable, and increases as T diminishes. Hence the ratio of p to p_1 increases rapidly as T diminishes, and by evaporating all the gases from the solid state, and keeping the solid at as low a temperature as possible, the gas first removable at the lowest pressure consists in by far the greatest part of that which has the lowest boiling-point, which in this case is nitrogen, and is succeeded, with comparative abruptness, by the gas which has the next higher boiling-point. In this way the nitrogen and oxygen are removed without the necessity of sparking or absorption. The change from one gas to another is easily detected by examining the spectrum in the sparking tube, and the reservoirs into which the gases are pumped can be changed when the spectrum changes, and the fractions separately stored. Or, if several sparking tubes are interposed in such a way as to form parallel communications between the tubes b and e, any one of them can be sealed off at any desired stage of the fractionation.

The variation of the spectra of both xenon and krypton with variation in the character of the electric discharge is very striking, and has already been the subject of remark, in the case of krypton, by Runge, who has compared krypton with argon in its sensitiveness to changes in the electric discharge. Runge distinguishes krypton rays which are visible without a jar and those which are only visible with a jar discharge. The difference in the intensity of certain rays, according as the discharge is continuous or oscillatory, is no doubt very marked, but, with rare exceptions, we have found that the rays which are intensified by the oscillatory discharge can be seen with a continuous discharge when the slit of the spectroscope is wide. Runge used a grating, whereas we have, for the sake of more light, used a prism spectroscope throughout, and were therefore able to observe many more rays than he.

There is one remarkable change in the xenon spectrum produced by the introduction of a jar into the circuit. Without the jar xenon gives two bright green rays at about λ 4917 and λ 4924, but on putting a jar into the circuit they are replaced by a single still stronger ray at about λ 4922.† In no other case have we noticed a change so striking as this on merely changing the

* A Paper read before the Royal Society, June 20, 1901.

† This line is almost identical with a strong helium line, but the yellow line of helium was not seen.

character of the discharge. Changes of the spectrum by the introduction of a jar into the circuit are, however, the rule rather than the exception, and there are changes in the spectrum of krypton which seem to depend on other circumstances. In the course of our examination of many tubes filled with krypton in the manner above indicated, we have found some of them to give with no jar the green ray λ 5571, the yellow ray λ 5871, and the red ray λ 7600 very bright, while other rays are very few, and those few barely visible. Putting a jar into the circuit makes very little difference; the three rays above mentioned remain much the brightest, nearly, though not quite, so bright as before, and the blue rays, so conspicuous in other tubes, though strengthened by the use of the jar, are still very weak. In other tubes the extreme red ray is invisible, the rays at λ 5571 and 5871 absolutely, as well as relatively, much feebler, while the strong blue rays are bright, even brighter than the green and yellow rays above named. In one tube the blue rays could be seen, though not the other. This looks very much as if two different gases were involved, but we have not been able to assure ourselves of that. The case seems nearly parallel with that of hydrogen. There are some hydrogen tubes which show the second spectrum of hydrogen very bright, and others which show only the first spectrum; the second spectrum is enfeebled or extinguished by introducing a jar into the circuit, while the first spectrum is strengthened; and the conditions which determine the appearance of the ultra-violet series of hydrogen rays have not yet been satisfactorily made out.

It is to be noted that putting the jar out of circuit does not in general immediately reduce the brightness of the rays which are strengthened by the jar discharge. Their intensity fades gradually, and is generally revived, more or less, by reversing the direction of the current, but this revival gets less marked at each reversal until the intensity reaches its minimum. The rays strengthened by the jar discharge also sometimes appear bright, without a jar, on first passing the spark when the electrodes are cold, and fade when the electrodes get hot, reappearing when the tube has cooled again. Moreover, if the discharge be continued without a jar, the resistance in the krypton tubes increases rather rapidly, the tube becomes much less luminous, and finally refuses to pass the spark. With an oscillatory discharge the passage of the spark and the brightness of the rays are much more persistent. This seems to point to some action at the electrodes, which is more marked in the case of krypton than in that of xenon.

The wave-lengths of the xenon and krypton rays in the accompanying tables were determined, in the visible part of the spectrum, with a spectroscope having three white flint-glass prisms of 60° each, by reference to the spark spectrum of iron, except in the cases of the extreme red ray of krypton, which was referred to the flame spectrum of potassium, and its fainter neighbour, which we saw but did not measure. The indigo, violet, and ultra-violet rays were measured in photographs, taken with quartz lenses and two calcite prisms of 60° each. The spectrum of the iron spark was photographed at the same time as that of the tube, the former being admitted through one-half of the slit, and the latter through the other half.

The xenon spectrum is characterised by a group of four conspicuous orange rays of about equal intensities, a group of very bright green rays of which two are especially conspicuous, and several very bright blue rays. The only list of xenon rays we have seen is that published by Erdmann, with which our list does not present any close agreement except as to the strongest green lines. The number of xenon rays we have observed is very considerable, and some of them lie very near to rays of the second spectrum of hydrogen, but inasmuch as these rays are more conspicuous with a jar in circuit than without, which is not the character of the second spectrum of hydrogen, and, moreover, many of the brightest of the hydrogen rays are absent from the spectrum of the tubes, we conclude that these rays are not due to hydrogen.

Certain rays, which we have tabulated separately, have been as yet observed in only one tube; they include a very strong ultra-violet ray of unknown origin, and one either due to some substance other than xenon, or to some condition of the tube which has not been repeated in the other tubes.

Our krypton rays agree much more closely with Runge's list, but outnumber his very considerably, as might be expected when prisms were used instead of a grating. Prisms, of course, cannot compete with gratings in the accuracy of wave-length determinations. We think that the krypton used by Runge must have contained some xenon, and that the rays for which he gives the wave-lengths 5419·38, 5292·37, and 4844·58 were really due to xenon, as they are three of the strongest rays emitted by our xenon tubes, and are weak in, and in some cases absent from, the spectra of our krypton tubes.

Tables of the Approximate Wave-lengths of Xenon and Krypton Rays.

Rays observed only with a Leyden jar in circuit have an * prefixed, those observed only when no Leyden jar was in circuit have a † prefixed.

The intensities indicated are approximately those of the rays when a jar is in circuit, except in the case of the two rays to which a † is prefixed, which are not seen when a jar is in circuit. Rays which are equally intense whether a jar is in circuit or not have a ‖ prefixed to the number indicating their intensities; those which are less intense with a jar than without have a < prefixed to the number expressing their intensities. The rest are, in general, decidedly more intense with a jar than without.

Xenon Rays.

Wave-lengths.	Intensity.	Wave-lengths.	Intensity.
*6596	4	5439	3
* 14	1	20	10
6472	‖1	5372	6
6358	1	* 68	1
45	3	39	6
20	‖1	13	1
02	1	09	1
6278	3	5292	10
71	3	62	2
6183	‖1	60	2
81	‖1	40	—
66	‖1	27	1
6097	6	02	1
51	6	5192	6
36	5	89	3
5976	6	85	3
72	—	79	3
46	2	26	3
35	<1	23	1
06	1	07	3
5895	‖1	5080	2
76	‖1	68	5
56	‖1	52	1
25	2	45	6
17	—	25	<1
5777	4	4988	4
59	4	72	2
51	5	† 24	†4
27	4	* 22	8
20	4	† 17	†4
00	6	4890	3
5668	4	87	—
60	1	84	4
17	—	83	—
09	1	76	4
5583	1	44	10
73	1	30	‖1
32	4	23	3
5473	3	* 18	3
61	3	07	<1
* 51	1	4793	1

Wave-lengths.	Intensity.
4787	2
79	2
69	2
40	1
34	<1
31	1
23	1
14	1
4698	||3
4677 to 4668	Band of close lines.
52	4
34	2
24	<2
16	3
02	8
4592	3
86	||5
77	3
56	2
45	3
41	3
35	2
25	||5
22	1
00	||1
4486	1
81	5
71	2
62	10
49	6
40	1
34	2
15	8
07	3
4396	4
93	4
86	3
75	4
69	4
56	1
43	1
37	3
31	10
22	3
11	3
4297	3
86	3
72	3
69	3
63	2
51	3
45	10
39	8
27	1
23	5
15	10
14	6
09	8
04	||1
01	1
4198	1
93	||6
81	10
76	1
72	1
63	3
59	3
46	3
42	1
32	2
21	1
12	2
09	6

Wave-lengths.	Intensity.
4106	3
00	2
4099	3
93	1
79	<1
74	1
60	1
58	6
50	6
44	1
43	1
37	6
29	1
25	3
21	1
02	3
3994	2
91	3
86	1
81	1
75	1
73	2
57	||1
55	4
51	<6
44	3
39	1
26	1
23	6
15	1
08	4
06	1
03	1
3894	3
85	3
80	3
77	3
70	2
62	2
58	2
55	1
50	2
49	1
42	4
29	1
26	1
24	1
15	1
11	3
07	1
01	1
3792	1
87	1
83	1
81	6
76	3
73	1
70	1
66	1
63	2
62	1
57	1
46	3
37	1
31	2
21	3
17	2
12	2
08	1
3689	1
77	3
73	2
64	1
62	2
58	1

Wave-lengths.	Intensity.
3655	2
50	1
45	6
41	2
32	2
24	10
16	1
13	4
10	2
07	4
02	1
3597	3
84	8

Wave-lengths.	Intensity.
3580	8
65	4
56	3
53	5
43	6
23	4
10	2
04	1
01	4
3468	2
61	1
54	1

Wave-lengths of Rays of Unknown Origin observed in the Spectrum of one Tube containing Xenon but not present in the Spectrum of other Tubes.

Wave-length.	Intensity.
4589	—
4071	1
67	1
63	—
11	1
3998	1

Wave-length.	Intensity.
3890	1
72	1
3797	5
41	4
3684	10
3573	2

Krypton Rays.

Wave-lengths.	Intensity.
7600	8
‡7587	1
6771	1
6578	1
42	3
11	2
6487	3
58	<1
51	3
20	<4
6305	3
6170	2
6095	1
82	1
56	2
21	1
11	2
5992	3
5873	1
71	<10
5771	2
53	2
5690	5
82	5
50	1
32	1
5571	<10
03	3
53	1
44	1
23	2
06	2
00	2
5483	1
46	2
29	1
24	1
03	1
5319	1
05	1
5278	1
29	1
18	1
15	1
09	5
03	1

Wave-lengths.	Intensity.
5186	1
72	1
66	5
43	4
26	6
5087	3
78	1
73	2
57	3
34	1
23	4
14	||2
4980	1
60	1
46	1
03	2
4847	2
45	2
33	5
26	3
12	3
4766	10
63	3
39	10
4694	3
80	5
59	8
50	1
35	6
20	8
15	6
10	3
4598	1
93	2
83	4
77	8
25	3
05	||2
4490	1
75	6
64	||3 pair
54	||1
37	6
32	6
23	2
00	1

‡ This is taken from Runge's number for the wave-length, omitting the fraction.

Wave-length.	Intensity.	Wave-length.	Intensity.
4387	3	3862	1
76	3	59	1
63	2	58	1
56	12	47	1
23	2	44	2
20	‖8	42	1
19	‖3	39	1
18	3	37	2
01	7	17	2
4293	10	06	2
83	‖3	05	3
74	‖4	3784	10
69	3	79	8
60	1	72	4
56	1	59	2
51	5	55	6
37	4	46	6
4185	3	42	6
72	1	36	3
45	8	34	4
40	2	22	5
19	3	19	10
09	6	15	1
4099	8	3691	1
89	8	87	5
65	7	81	7
58	6	70	7
45	4	67	1
38	2	64	3
08	2	61	3
05	1	54	10
3997	3	49	3
94	6	38	4
88	2	32	10
65	1	24	1
55	2	08	6
39	1	00	6
28	3	3590	3
21	8	74	1
18	2	54	2
13	6	45	6
07	6	03	2
01	1	3489	2
3896	3	70	1
76	7	60	3

AN IMPROVED METHOD OF PRODUCING ULTRA-VIOLET-SENSITIVE PLATES.*

By V. SCHUMANN.

(Continued from p. 41).

Development of the Latent Image.—Of all the developers that I have tried, the pyrogallic-soda developer has been most satisfactory.

Freshly-prepared plates can take equal parts of both solutions without the addition of water usual for dry plates. For raising the intensity of the negative, which is usually low in the beginning, a water solution of potash (1 : 3) may be used, being added to the developer in amount from a few drops to half the volume of soda. A few drops of potassium bromide (1 : 10) render the plate transparent and cause a rise of intensity. It must be remembered that potassium bromide considerably retards the appearance of the picture, and that it only acts with full power when it is present from the beginning of development. Potassium bromide added during the development is nearly without action.

Cold developer acts similarly to potassium bromide. The warmer the former is, the sooner and more complete is the appearance of the image, while very cold solutions lead to negatives richer in contrast.

* *Annalen der Physik*, 1901, vol. v.

I prefer to start developing with the bath as cold as possible, and warm it as soon as the most active lines have appeared. I manage the warming in the simplest manner —by rubbing the bottom of the bath with the flat of the hand, which gains the desired effect without trouble. In many cases very clear and powerful negatives are produced with a bath very rich in potassium bromide, followed by a second containing no potassium bromide after the first lines have appeared.

I proceed otherwise when dealing with single exceedingly fine lines, or with dense groups of lines differing but slightly in energy. In this case I make a preliminary exposure with a very narrow slit, from 0·001 m.m. downwards. If this does not suffice, which is generally the case, I repeat it, changing the time of development to correspond to the desired result—sometimes shortening, sometimes lengthening it. If the second operation is not successful, a third will generally suffice. It is advisable to expose for a sufficiently long time, but in no case to carry the development further after the lines have appeared. For the analysis of extensive spectra with large energy differences this method is useless, because the slit aperture of the collimator, which is of necessity narrow, considerably enhances the most powerful lines, in which rays of very different activity occur in contiguity, and singles them out before the weaker lines have attained the capacity for development.

Older plates can seldom bear developing with undiluted solutions without becoming fogged. For these, it is necessary to add water (1 volume pyrogallol, 1 volume soda, 1 to 2 volumes water), as well as to increase the quantity of potassium bromide (1 to 3 drops of 1 : 10 potassium bromide per c.c. undiluted pyro-soda solution). Prescriptions for general use cannot here be given. The composition of the developer must be regulated each time by the nature of the experiment and by the age of the plate.

The development takes place with fresh plates, and without potassium bromide in the developer, in two to three minutes, with potassium bromide in three to four minutes, while it requires twice or three times as long with plates one to two months old, on account of the necessarily weaker solutions and the increase in potassium bromide.

I develop small plates (13 × 37 m.m.) in an evaporating dish, pouring the mixed solution directly on to the plate. It is advisable to transfer the wet plate from one bath to the other with suitable tongs, on account of the fragile nature of the film. I use tongs with hooked ends of hard ndiarubber, which clip the plate at the edges. It is best to leave plate and pincers joined together until the negative is dry.

The appearance of the picture is seen on a white foundation better than on a coloured, and in the same way white dishes are preferable to all others.

The illumination of the dark room may be the same as that for the ordinary dry plate. I always work with the brown light, which is photographically more inactive than the red, and soft to the eyes, which cannot be said of the other.

Fixing, Washing, and Drying.—When development is finished, the basin containing the negative is filled up several times with water, and the plate then immersed in a solution of sodium hyposulphite (1 : 3 to 1 : 4), in which the silver bromide dissolves in a few seconds. In an acid fixing-bath the solution takes longer. In the short period of fixing, the ultra-violet plate differs advantageously from the ordinary dry plate. Productions of lasting value are better preserved by dipping for a few seconds in a second fixing-bath after rinsing the surface with water. In order to wash out the fixing, the plate is placed for about two minutes upright in a stream of water—not so strong as to spoil the film—then sprayed carefully with distilled water, and finally supported on a platform, free from dust, in such a manner that the water can all drain off at one corner. The washing may be conducted in standing water instead of flowing; this is to be recommended in the case

of large sizes. I use for this purpose suitable beakers and evaporating basins. If the film is placed downwards, it is fully washed in ten to fifteen minutes with four or five changes of water. It is freed from its soluble salts, on account of its thinness, more readily than the ordinary dry plate. Drying requires ten to fifteen minutes in the fairly warm still air of the room.

It is not necessary to treat every plate with the care above described, but it is essential when the greatest purity is required. In general, where little dry-spots are no disadvantage,, the process can be made much shorter. The plate, after being removed from the first fixing-bath, is held for two minutes in a stream of water and then dried in the neighbourhood of a stove (not too hot), over a lamp or near its cylinder, for which a few minutes suffices.

The Dry Negative.—The image is grey-brown, in transmitted light black-grey with a transparent ground. This transparency makes the deposition of dust particles much more noticeable than with other negatives, which always have a thick ground.

A spectrum on the ultra-violet-sensitive plate may be very greatly enlarged, on account of the extraordinary fineneness of its lines. The spectra obtained from a very narrow slit give clear pictures enlarged a hundred times. The ordinary dry plate cannot bear enlargement to such an extent, the reason for which can only lie in the greater thickness (five times) and in the relatively greater proportion of gelatin in the sensitive film.

(To be continued).

CONTRIBUTIONS TO THE SCIENCE OF NITROCELLULOSE.*

By G. LUNGE and J. BEBIE.

(Continued from p. 42).

A. *Influence of Water upon the Process of Nitration* (continued).

With 16·6 per cent water (experiment 5), we get a completely soluble product, and with this arrive at the group of the collodion cottons. The action of the water becomes increasingly more intense; there is a rapid decrease of the nitrogen percentage with increase of the water percentage from 18 per cent onwards. The group of soluble nitrocelluloses between 170 and 196 c.c. is bounded with a difference of water content of only 4 per cent, and this through the interval of about 16·5—20·5 per cent. Between experiment 7 and 8 lies octonitrocellulose of commercial importance (typical collodion cotton), with a nitrogen content of 177·2 c.c. By reference to the curve of which the ordinates give c.c. NO per 1 grm., and abscissæ water percentage of the nitration mixture), the corresponding water content should be 19·5 per cent. This was confirmed by experiment, for a nitration mixture containing 19·42 per cent water led to the desired stage of nitration, which is always to be obtained in this manner.

We must now turn to the communications published by Wyss-Naef on the manufacture of cotton-silk at Besançon. According to this the collodion cotton is produced by treating cellulose for four to six hours with a mixture of 85 parts sulphuric acid, and 15 parts fuming nitric acid. Concentrated sulphuric is not expressly mentioned, but only that can be intended as mention is afterwards made of the great attraction for water of the nitration mixture. Again, a technical method exacts for reasons of economy, that if, in a mixture of acids, one of the acids is concentrated, and the other must be diluted to a certain extent, one should use the dearer nitric acid in the concentrated form, but the cheaper sulphuric in the dilute form. But the specific gravity of the nitric acid is given as 1·52; hence for sulphuric acid we must understand concentrated acid.

* *Zeitschrift fur Angewandte Chemie*, 1901, Heft 20.

These statements are revised in the book, "The Artificial Silk," recently published by Dr. Süvern. But Lunge and Weintraub were not able to obtain collodion cotton in this manner. The body prepared by them according to the prescription of Wyss-Naef contained only 19 per cent of soluble matter, and moreover nitration was not complete, for by means of the polarisation microscope unchanged cellulose was seen. The nitration was carried out at the temperature of the room. But we have since ascertained that nitration is conducted at a somewhat higher temperature in the art-silk manufacture. As the sulphuric acid is present in great excess it was not ascertained that this acid mixture would lead to materially different results on raising the temperature. Hence, some experiments were made in this direction for the completion of those of Lunge and Weintraub, but, as is shown by the following table, with equal ill-success :—

Temp.	Time of nitration.	C.c. NO per 1 grm.	Solubility.	Increase.
30°	4 hours	199·89	17·14	160·2
40°	7 hours	209·20	15·54	143·1

The nitration products obtained are only soluble to a small degree, but here, on the contrary, the nitration is complete in contrast to nitration at the ordinary temperature. The cellulose remained unchanged. In polarised light the fibres appeared light steel-blue.

In the above-named communications the nitration is characterised as complete when all the fibres reflect blue. But it must be added that nitrocelluloses with a nitrogen content below 190 c.c. (and these are they which come into consideration here), never showed a blue illumination. The statements of Wyss-Naef must also be taken with caution.

We now return to the discussion of the first series of experiments. If the nitrogen content falls below 160 c.c. the solubility again decreases. The nitration stages from hexanitrocellulose (C_{24}...) downwards are insoluble in ether-alcohol. This agrees with the statements of Vieille, in contradiction, however, with those of Eder, according to whom di- and tri-nitrocellulose (C_{12}...) were soluble. Eder obtains these products by treating cellulose with very hot acid mixtures. But in this the cellulose molecule does not remain intact, which is evident from the fact that, from the dinitrate thus produced, no cellulose can be regenerated with ferric chloride. With a water content of about 25 per cent and upwards nitration is not further completed after twenty-four hours' reaction. For example, in experiment 12 the acid mixture was kept on the cellulose for three days; but there always remained some unconverted cellulose. By the method of Lunge and Weintraub the amount of this comes out at 4·1 per cent. Calculated from material freed from cellulose the nitrogen content was 108·12 c.c., which would correspond to tetranitrocellulose. But (for reasons to be mentioned later), the nitrogen determination cannot be exact in this case, and hence the figures must only be regarded as an approximation.

With a further increase of water the nitration effect is very slight. At first there is still something of this, but afterwards the products which result have the properties of oxycellulose; they are completely or partially soluble in dilute alkalis, and can be recovered from the solution by acids or alcohol; they become deeply coloured with basic colour agents, reduce Fehling's solution, and form phenylhydrazine compounds.

As already remarked, the time of nitration during these experiments lasted twenty-four hours, and the temperature was that of the room.

For producing collodion cotton on a large scale a raised temperature was adopted in most cases. This is in general advantageous, because it increases the speed of reaction. A few experiments, carried out at a higher temperature and a correspondingly shorter time of nitration, showed that the results of the last series of experiments are directly related to these nitration conditions.

The following table shows the results obtained with the acid mixture used in experiment 7 :—

Expt.	Time of nitration. Hours.	Temperature.	C.c. NO per 1 grm.	Solubility in ether-alcohol.	Increase.
1.	4	17°	183·54	95·60	155·1
2.	24	17°	184·78	99·81	156·2
3.	4	40°	183·40	99·58	148·1
4.	4	60°	172·48	99·82	52
5.	¼	60°	182·80	99·71	146·7

With this nitration mixture, even at the temperature of the room, nitration was complete after four hours (Expt. 1). The product is of greater increase than that produced at 40°; on the other hand, the solubility in ether-alcohol is less easy and complete. By raising the temperature to 60° partial denitration quickly set in. After four hours' reaction the nitrogen content sank to 172·48 c.c. In this experiment the structure of the cotton was entirely destroyed; hence the fine fibrous pulp was, for the purpose of washing, poured, together with the acid mixture, into a great quantity of cold water, after which the nitration product was treated in the usual way. The increase rapidly diminished. Secondary reactions set in through the hot acid mixtures. Experiment 5 shows that a higher nitration is next effected, in which the time of nitration was confined to a quarter of an hour; therefore a partial denitration again takes place through the action of the hot acid mixtures. Hence the conditions of this experiment yield the product in the shortest time. But the nitrocelluloses produced at so high a temperature are said not to give collodion capable of being spun (as we learn from a private communication of Dr. Brönnert), and are hence useless for the purposes of the artificial silk manufacture. The structure of the cotton suffers a great change on nitration with increasing water content of the acid mixtures. It remained almost unchanged up to the proportion of about 15 per cent water; from about 18 per cent onwards the fibres appeared somewhat drawn together. With higher percentages of water the structure became almost entirely destroyed; the fibres break up into small particles, and become matted into clotted masses. This destructive action reaches its maximum with 23—25 per cent. It is these compact products that offer greater resistance to the action of sulphuric acid, on account of the small amount of surface. With more dilute acid mixtures the fibres remain intact, and are only split into smaller fragments on longer treatment.

This series of experiments gives us an idea of the great importance of the proportion of water contained in the nitration mixtures.

(To be continued).

ON THE

CIRCULATION OF SALT AND ITS BEARING ON CHEMICO-GEOLOGICAL PROBLEMS.

By WILLIAM ACKROYD, F.I.C., F.C.S.,
Public Analyst for Halifax.

The few observers who have practically gone into the question of chlorine distribution in the British Isles are aware that only isolated facts are on record; that we have not that fulness of information which could be utilised in constructing iso-chlors; that the chlorine in rainfall, more particularly in the neighbourhood of towns, is wildly variable, and has been studied in only a few cases, and therefore that it is a mistake for Prof. Joly to say we possess "very full information" on any one of these points. It is also a mistake, arising from hasty reading perhaps, for him to impute to me the style of reasoning which he gives in the sixth paragraph of his communication (Chem. News, vol. lxxxiii., p. 301); this is based on a misunderstanuing of the method I have devised of arriving at the ratio of earth-salt to sea salt in river waters.

May I add for Prof. Joly's information that it is assumed all the combined chlorine is equally diffused throughout the limestone, and that for every degree of hardness acquired by the water a proportionate amount of combined chlorine enters into solution; at the same time silica, alumina, and organic matter, &c., will be taken up either in solution or suspension. Let us leave Craven.

On Combined Chlorine as a Measure of Solvent Denudation.

No less remarkable results are obtained by turning to other regions. I will take another example, and let it be noted that this instance refers to some 13,300 square miles of the earth's surface, a somewhat larger sample than part of the watershed of the Aire

The waters of Connecticut and Massachusetts contain combined chlorine; the element has been derived either in whole or part from the rock bed over and through which the water passes, or in whole or part from the rain. Now the rocks, whether felspar, serpentine, or dolomite, collected by the U.S. Geological Survey from Blandford, Middlefield, Granville, Rowe, Russel, Chester, and over a score of other places, contain no chlorine (see *Bull. U.S. Geol. Survey*, No. 148). Therefore the chlorine must have descended with the rains. The gradual increase in the iso-chlor figures as the sea-coast is approached is a final demonstration of the marine origin of the chlorine. Let it then be noted that, deduct what we may from the chlorine figure for any water in these regions, and what is left is still representative in the largest degree possible of cyclic sea-salt. Herein I take it lies the fallacy of Prof. Joly's calculation on p. 302, where he deducts 0·1 per 100,000 as "the average amount of chlorine carried by rains to the rivers after evaporation" from 0·3 parts per 100,000, "the amount of chlorine appearing in the mean river water." I may also be permitted to point out a discrepancy which must be a source of confusion to those who are trying to get at the root of the matter. In the *B. A. Report* for 1900, p. 721, we are told "the proportion of Na in Prof. Joly's average river water is only 5·73 per million." The chlorine equivalent of this is 0·88 part per 100,000. From 0·3 to 0·88 is a difference of nearly 266 per cent. One turns in vain to Appendix I., p. 65 (*Trans. Roy. Dub. Soc.*, 1899), for enlightenment on the matter.

Now as chlorine is the most important of all the elements combined together in the substances forming the dissolved matters of the ocean, it would be legitimate, if it were possible, to take the chlorine contents of the ocean and divide by the annual chlorine increment yielded by the rivers, after all necessary corrections, to get at the age of the earth. Mr. Millard Reade has used calcium sulphate; Prof. Joly, sodium; then why not chlorine? It will have become abundantly clear by now that in using chlorine on the assumption of uniformity of the work of solvent denudation our divisor would be relatively so small as compared with the numerator as to give a quotient too large to obtain scientific credence. The example just given is striking proof of this, and, however liberal one may appear to be in an allowance for salt transported from the sea and back again, the needs of the case do not seem to be adequately met. Much mathematical discretion may be exercised in fixing this allowance, for while 50 per cent does not much impair results, 70 per cent begins to make them look bad, and things are going worse out of all proportion when 90 per cent has been wrung out of an unwilling opponent.

Evaporation.

In further considering the possibility of using a chlorine divisor it would be necessary to very particularly consider those parts of the earth's surface, by no means inextensive, where rivers rise in or flow through the torrid zone. The excessive evaporation must be taken into account. In the case of the Nile I have already pointed out that there is a variation of something like 400 per cent in the

chlorine figure, and other rivers like the Niger and Congo must similarly vary. Has Prof. Joly made allowance for these seasonal variations? And did Sir John Murray in sampling his average river waters provide fully for them? Because it goes without saying that, as chlorine combined with sodium forms the great constituent of the ocean, the latter element must share in these restrictions to a very important degree.

The Great Storm of 1839.

The public interest aroused in the subject of salt circulation by my paper has led to many reminiscences being communicated to me. One to the effect that early in 1839 the window-panes in this town, facing west, were *thickly* encrusted with salt during a storm has been confirmed by reference to contemporary records. An account of the storm is given in a book entitled "A Narrative of the Dreadful Disasters occasioned by the Hurricane which visited Liverpool and Various Parts of the Kingdom on the Nights of Sunday and Monday, January 6th and 7th, 1839." It is a reprint from the pages of the *Liverpool Mercury*. The following are the passages confirming local verbal narrative:—

"It is a singular fact that trees about Huddersfield during the storm on Monday appeared as if covered with hoar-frost, but as it did not freeze it led to an examination, when it turned out that this was a briny deposit which the wind had probably brought from the Irish Sea."

Under the heading "Longton" (near Preston?) there is this passage, "Twelve o'clock at noon, wind W. The trees and hedges appear as covered with hoar-frost by reason of particles of salt."

On the Origin of the Saltness of the Dead Sea.

Storm effects like these enable one to realise that with extreme meteorological conditions, such as have admittedly obtained in the past history of the Jordan watershed, it may have been no uncommon thing for Palestine to be drenched with sea-salt by the prevalent westerly gales, in which case a more important contribution towards the saltness of the Dead Sea would be made than could be furnished by the widely distributed limestone rocks. The quieter circulation of salt which is in progress in calmer times would probably contribute a no less important share.

Prof. Joly raises no valid objection to such a theory when he points out that wide differences exist in the composition of the waters of salt lakes; indeed it would be strange if there did not! Each case must be studied in connection with its supposed causes. No good can come, at the present stage of the inquiry, of comparing the Dead Sea with the Great Salt Lake; such a comparison is illogical. To confine one's attention to the former I have shown that the ratio of the closely related ions Cl and Br is practically the same for the Dead Sea and the Mediterranean, and such a comparison was made because it appeared not unlikely that whatever vicissitudes one of the waters might have suffered, two such elements on account of their close kinship would be likely to preserve their proportions if the salts of one of the waters were derived either altogether or very largely from the other. The vicissitudes referred to are suggested by the question, Would the wind borne salts of the Mediterranean, brought down by rain and lodged in a locality of higher evaporation, undergo a concentration which would tend in time to a "salting out" or precipitation of some of the dissolved bodies, and the production of a "mother-liquor" similar to the waters of the Dead Sea? From what we know of the history of such mixed solutions we are entitled to answer in the affirmative. In the manufacture of bay salt from Mediterranean sea-water the bittern bears interesting points of resemblance to Dead Sea water, and no doubt some individuality has been superadded to the latter by its limestone gathering grounds.

Several other matters arise in Prof. Joly's criticism which I think will be fully answered by a thoughtful reperusal of my original paper.

THE RATE OF NITRIFICATION OF SOME FERTILISERS.*

By W. A. WITHERS and G. S. FRAPS.

(Concluded from p. 46).

Rate of Nitrification.

The experiments to determine the relative rate of nitrification were carried out as follows:—The fertilising materials were those sent out by the referee of the Association of Official Agricultural Chemists for 1900, to test the methods for determining the availability of nitrogen. A sandy clay soil from a pasture was sifted through a coarse sieve (6 meshes to the inch), and a quantity of material equivalent to 0·6 grm. nitrogen was intimately mixed with 1000 grms. of the soil. The soil was then placed in precipitating jars, and kept in a dark closet, enough water being added to raise the percentage from 6·3 to 11·6 per cent. At suitable periods, three of the jars were weighed, and the estimated loss of water was replaced in all the jars. The temperature was 28—30° C., and the time was three weeks. When calcium carbonate was added, the amount was exactly sufficient to combine with the nitrogen of the fertiliser if the entire amount were converted to nitric acid. At the end of the experiment, the nitrates were leached out, and the amount determined by the Tiemann-Schulz method. The amount of nitrates found in a blank experiment was deducted from the total. The results are given in Table III.

On account of the surprisingly small percentage of ammonium sulphate nitrified in the first series, the experiments with cotton-seed meal and ammonium sulphate were repeated, the time being twenty-six days, the temperature 23—26° C., and the sample moistened as before. The soil was taken from the same pasture as in the first series, but differed from it somewhat, as is shown by the fact that it contained 0·1641 grm. nitrogen as nitric acid per kilogrm., whereas the former contained only 0·0595 grm.

Rate of Nitrification and Availability of Nitrogen.

We have selected, and give below (Table III.), the results obtained by vegetation tests with oats and Hungarian grass by Jenkins and Britton (*Conn. State Station Report*, 1897, 357), and those obtained by Bizzell in the laboratory of this Station with the pepsin-hydrochloric acid method, and the neutral permanganate method, the materials being those used in these nitrification experiments.

The order of availability as determined by the neutral permanganate method, and by the vegetation experiments, is the order of nitrification, except in the case of ammonium sulphate. The pepsin-hydrochloric acid method places bone next to blood, and above cotton-seed meal, where it does not belong.

The mechanical condition of the material would, of course, have great effect on the rate of nitrification. It is quite possible that the organic fertilisers contain two or more nitrogen compounds of different degrees of susceptibility to the nitrifying organisms. Bone was nitrified to the extent of 18·9 per cent in three weeks, and only 21·7 per cent in six weeks.

Effect of Calcium Carbonate.

Taking the quantity of nitrates formed without the presence of calcium carbonate as 100, the quantity formed with it present was, with dried blood, 158; cotton-seed meal, 162; dried fish 153; tankage, 133; bat guano, 160; bone (three weeks), 88; bone (six weeks), 80; ammonium sulphate, 2390; ammonium sulphate (Series II.), 959. This effect may depend on the quantity of bases present in the material. The rate of nitrification of bone, which contains large quantities of calcium salts, is actually

* Contribution from the North Carolina Agricultural Experiment Station. From the *Journal of the American Chemical Society*, xxiii., No. 5.

Table III.

	Rate of nitrification.				Availability.		
	Without.		With $CaCO_3$.		Soluble.		
	Per cent.	Rank.	Per cent.	Rank.	$KMnO_4$.	Pepsin.	Vegetable test.
Series I.							
Dried blood	34·8	100	54·9	100	94·4	94·7	73·3
Cotton-seed meal	33·9	97	54·8	100	91·1	91·1	64·8
Dried fish	30·3	87	46·5	85	88·7	67·3	63·9
Tankage	26·2	75	34·8	63	88·3	56·4	49·4
Bat guano	22·4	64	35·8	65	75·1	56·4	—
Bone	18·9	54	16·6	30	64·2	92·3	16 7
Bone (six weeks)	21·7	—	17·4	—	—	—	—
Ammonium sulphate	1·3	4	31·1	55	100	100	—
Sodium nitrate	—	—	—	—	100	100	100
Series II.							
Cotton-seed meal	26·7	—	—	—	—	—	—
Ammonium sulphate	3·4	—	32·6	—	—	—	—

decreased by the addition of calcium carbonate, while that of ammonium sulphate is increased enormously. These results show the beneficial influence of lime in rendering nitrogenous fertilisers available, and explain in part why lime is so beneficial to many crops.

When ammonium sulphate is used as a fertiliser, it would be advisable to add calcium carbonate at the same time, in many cases.

Nitrification of Ammonium Sulphate.

As regards ammonium sulphate, in a soil deficient in lime, it is nitrified less readily than any other of the fertilising materials tested. In the soil to which calcium carbonate has been added, the rate of its nitrification still falls below that of cotton-seed meal, blood, and dried fish, and was in one series less, the other greater, than tankage and bat guano, but the average was below. In Bonâme's experiments ammonium sulphate was nitrified during the first and second months less rapidly than any of the other fertilising materials used (blood, oil cake, guano), whether calcium carbonate was added or not. On the contrary, the experiments of Müntz and Girard (presumably in a soil containing calcium carbonate), place ammonium sulphate at the head of all the fertilising materials tested (blood, flesh meal, poudrette, roasted leather, leather chips).

There are three possible ways to account for the slow rate of nitrification of ammonium sulphate.

1. Ammonium sulphate may hinder the action of the nitrifying organism. The soil in question contained 2·5 grms. ammonium sulphate dissolved in 100 grms. of soil water. It is known that various salts will retard the nitrifying activity of the organisms if present in too large quantity. Deherain found that common salt began to be harmful when more than 0·1 per cent of the weight of the soil was added, and with larger quantities nitrification almost ceased. Large additions of sodium nitrate also decrease the rate of nitrification.

This explanation will not account for the beneficial action of calcium carbonate, for if double decomposition takes place, the ammonium carbonate formed is more of a hindrance to the germs than the ammonium sulphate.

The assumption that ammonium sulphate hinders the action of the nitrifying organism would explain the low rate of nitrification of ammonium sulphate that we have obtained. It would also explain the results of Bonâme (already cited), according to which ammonium sulphate is nitrified very slowly indeed the first and second months, and very rapidly the third. In direct contradiction to the above hypothesis, however, would stand the experiments of Müntz and Girard, who found that, in thirty days, ammonium sulphate was nitrified to a greater extent than dried blood, &c., and those of Th. Schloesing (*Central-Blatt. Agr. Chem.*, 1890, xix., 1, abs.). The latter found that at the end of fifty-six days ammonium chloride added to a soil at the rate of 3·58 grms. per kilo. (1·8 grms. per 100 c.c. of soil water), was almost completely nitrified, and the same occurred with ammonium sulphate at the rate of 2·7 grms. per kilo. (1·4 grms. per 100 c.c. soil water), in twenty-two days, and ammonium carbonate at the rate of 0·53 grm. ammonia per kilo. in twenty-eight days. The soil contained 19·4 per cent water.

These difficulties might be explained by supposing that the ammonium sulphate affects the nitrifying germs less in some soils than in others, either on account of the different character of the soils (power of fixing ammonia, &c.), or the presence of different kinds of nitrifying organisms.

If the ammonium sulphate is detrimental to the nitrifying organisms, the same kind of action would take place when it is used as a fertiliser, though perhaps to a less degree. Each lump of the salt would become a centre from which would diffuse a solution of ammonium sulphate, detrimental to the nitrifying organisms. The time required for this unfavourable condition to disappear, would depend on the rate of diffusion of the salt, soil, moisture, rainfall, &c.

2. The second explanation for the slow rate of nitrification of ammonium sulphate compared with the other materials, is that the nitric and sulphuric acids formed are detrimental to the nitrifying organisms, being only neutralised in part by the bases of the soil. When calcium carbonate is added, it neutralises the acids, with consequent acceleration of the change. This explanation is probably applicable, but does not explain all the facts, for if so, the addition of calcium carbonate would remove the unfavourable conditions, and place ammonium sulphate at the head of the list, which it does not do.

3. The third explanation is, that different soils contain different nitrifying organisms, some of which convert organic matter directly to nitrites, while others change ammonium salts to nitrites more readily. The nitrites are then converted to nitrates. In soils containing the first kind of organisms, and few of the second, organic matter would be converted to nitrites more rapidly than ammonium salts would be, as was the case in the experiments of Bonâme and those here described. In soils in which the second class of organisms predominate, ammonium salts would be nitrified more rapidly than organic compounds. This hypothesis would explain all the experiments here cited.

It appears very probable that all three of the explanations given above apply, and that all three are in operation, one exerting a greater influence in some soils than others. It is the purpose of this Station to continue the experiments on nitrification, with a view to test all the problems that may arise.

Conclusions.

1. The nitrification of blood takes place more rapidly

when it is mixed with a large quantity of soil than with a small quantity.

2. The order of nitrification in the soil used was, dried blood (most nitrified), dried fish, tankage, bat guano, bone, ammonium sulphate. Excluding the ammonium sulphate, this is the order of availability, as measured by vegetation tests and solubility in potassium permanganate.

3. When calcium carbonate was added to the soil, the nitrification was greatly accelerated, and the order became, dried blood, cotton-seed meal, dried fish, bat guano, tankage, ammonium sulphate, bone.

4. When ammonium sulphate is used as a fertiliser, in most cases it would be advisable to add calcium carbonate in some form also.

5. The low rate of nitrification of ammonium sulphate is probably due to the presence of organisms which nitrify organic compounds in preference to ammonium salts. The presence of the ammonium sulphate may also hinder the activity of the nitrifying organisms. The acids formed may also be a hindrance when no base is present to neutralise them. All three of these causes may be in operation at the same time.

CORRESPONDENCE.

THE DIRECT ESTIMATION OF CARBON IN METALS.

To the Editor of the Chemical News.

SIR,—I am obliged to Mr. McIntosh for his information relating to the sharp practices of the paint trade. This knowledge, however, does not appear to have especially qualified him to deal with the direct estimation of carbon in refractory alloys.

Unfortunately the worser kinds of red-lead were not preserved, and I am therefore unable to make any further examination of them in order to convince Mr. McIntosh that they were not merely "barytes dyed with a coal-tar colour." Their general behaviour during and appearance after fusion, however, favours the conclusion that they were mixtures of oxides of lead with a red colour. Moreover, one of these which gave a blank of 0·0674 on 10 grms. was in regular use in a neighbouring laboratory for the purpose of estimating manganese in steel by that process where permanganate is formed by boiling a nitro-sulphuric solution with red-lead. It can hardly be claimed that "barytes dyed with a coal-tar colour" will oxidise manganous salts to permanganate.

Even when red-lead consists substantially of lead and oxygen only it is rarely Pb_3O_4. It has been shown in a volume of the *Journal of the American Chemical Society* (for the year 1897, I think), to which I have no means of referring, that commercial red-lead almost invariably contains an excess of PbO over and above that needed to form $2PbO.PbO_2$. I imagine that this excess of PbO might be the cause of the blank, on account of the facility with which it takes up CO_2 from the air. This explanation of the blank, which occurs even when the possibility of trade trickery is eliminated, is the most obvious one.

As though halting in his conviction that red-lead free from CO_2 was easy to obtain, Mr. McIntosh banishes it altogether, and purposes to use lead chromate prepared on the spot. If he had ever actually tried this experiment he would know, even supposing the reagent were free from blank (?), that the whole of the carbon could not be got from a rich ferrochromium say, except at temperatures very much beyond those obtainable in the average combustion furnace. "Chromate of lead strongly fused and powdered is a much more effective reagent, but Mr. McIntosh would have to reject it "even if the blank were completely negative," because it certainly does not "dissolve instantaneously in a large excess of potash."

Perhaps Mr. McIntosh would find in practice, if he avoided the "know nothing and care less" kind of dealer, that more purposeful knowledge could be gained by a "blank" experiment than by the tests he mentions.

It only remains to point out that the blank referred to is the increased weight of the KHO bulb after ignition of the sample, and not the percentage of carbon calculated therefrom, as Mr. McIntosh has assumed.—I am, &c.,

HARRY BREARLEY.

Totley, near Sheffield,
July 29, 1901.

ESTIMATION OF AMMONIA IN ITS SALTS.

To the Editor of the Chemical News.

SIR,—Mr. Bennett Blackler in the CHEMICAL NEWS (vol. lxxxiii., p. 299) draws attention to what he calls a new method of indirectly estimating ammonia in ammoniacal salts.

It may interest him to hear that this is an old and well-known method: personally I was taught it twenty years ago by the late Dr. Dittmar in Anderson's College, Glasgow, and since then have constantly used it, more especially in the testing of sulphate of ammonia.

The following working details are much better for commercial sulphate of ammonia:—Weigh out 3 grms. of the sample, dissolve in water, in a porcelain basin, add methyl orange, neutralise with normal caustic soda, add 50 c.c. normal caustic soda solution, boil, and after cooling, titrate back with normal sulphuric acid. Each c.c. soda solution consumed corresponds to 17 m.grms. NH_3.—I am, &c.,

ALEXANDER BUCHAN.

13, Willowbank Crescent, Glasgow,
July 22, 1901.

THE TINTOMETER IN WATER ANALYSIS.

To the Editor of the Chemical News.

SIR,—Would any reader of the CHEMICAL NEWS be kind enough to acquaint me with his experience, if any, of using a tintometer in connection with water analysis for the purpose of estimating ammonia by means of Nessler's solution? Or, failing this, has a tintometer ever been used for this purpose?—I am, &c.,

E. R. DEACON.

AN INSPIRATION FROM THE IMMORTALS.

To the Editor of the Chemical News.

SIR,—Ordinary mortals are indebted to *L'Illustration* for a picture representing one of the "Forty Immortals," engaged in the "meditations, calculations, and experiments" which enabled him to "solidly build up organic chemistry on the positive basis of synthesis," and kodaked in the act of permitting "conquered matter to operate in a closed vessel," provided with a thermometer so delicate that he is reading it with a magnifying glass (at an angle of about 45°), while grasping it with his fingers at a point well below the top of the mercury column.—I am, &c.,

DIAZO.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 2, July 8, 1901.

New Derivatives of Benzylcamphor and of Benzylidene-Camphor.—A. Haller and J. Minguin.—The author's researches show that the non-saturated acid—

$$C_8H_{14}\begin{cases}CH=CH.C_6H_5\\COOH\end{cases}$$

which is produced when benzylidene-camphor is treated with hot hydrobromic acid or the bromated benzyl-camphor—

$$C_8H_{14}\begin{cases}CH.CHBr.C_6H_5\\CO\end{cases}$$

by potash or alcoholic ammonia, fixes a molecule of hydrobromic acid, giving the bromated acid—

$$C_8H_{14}\begin{cases}CH_2.CHBrC_6H_5\\COOH\end{cases}.$$

This acid when heated with an acetic solution of hydrobromic acid is transformed into the acid—

$$C_8H_{14}\begin{cases}CH_2—CH.OHC_6H_5\\COOH\end{cases}.$$

Manganic Phosphates.—V. Auger.—The author's researches were carried out chiefly on the violet solution which forms the product of fusion of manganese nitrate and phosphoric acid heated to about 210°. The molten mass, when dissolved in water and left for some days, deposits a rose-coloured crystalline crust, manifestly a mixture of two or three products. Herrmann analysed a portion of this crust and found it correspond to the formula $Mn_4P_6O_{21}.8H_2O$. The author isolates from the same mass a hydrated salt in a pure state, and finds it to have a formula differing from Hermann's only in the amount of water of crystallisation, $Mn_4P_6O_{21}.14H_2O$. This salt is certainly a pyrophosphate, for when treated in the cold by an alkali, it gives an alkaline phosphate which possesses all the reactions of pyrophosphoric acid. Manganic metaphosphate, MnP_3O_9, was also isolated from the crust and found to be anhydrous.

Action of Acid Chlorides on Methanal.—Louis Henry.—The author investigates the action of pentachloride and pentabromide of phosphorus on polymerised methanal, which action causes the latter to be transformed into $H_2C—Cl_2$ and $HCBr_2$. He also examines the action of acetyl chloride and bromide on the same body, an action which furnishes methylene chloro- and bromo-acetates—

$$H_2C\begin{cases}Cl\\C_2H_3O_2\end{cases} \quad \text{and} \quad H_2C\begin{cases}Br\\C_2H_3O_2\end{cases}.$$

Action of Vegetable Alkaloids on certain Indicators.—A. Astruc.—Vegetable alkaloids act on various indicators in a different manner, varying not only according to the group to which they belong, but also with the dissociating power of the liquid in which they are dissolved. As there exists a perfectly symmetrical relation between the thermometric constants and the alkalimetric or acidimetric constants, the results of the calorimetric determinations effected in various media, which are already in course of experiment, may be predicted.

Di-naphthoxanthene.—R. Fosse.—The author prepares the mono-chlor and mono-bromo derivatives and also an amine of di-naphthoxanthene in order to compare these bodies with the hydrochloric and hydrobromic ethers and the amine of the pretended binaphthyleneglycol. He discovers in these derivatives of di-naphthoxanthene curious properties about which nothing can be found up to the present time in chemical literature and no analogous examples amongst non-nitrated bodies.

Nitration Product of Acetylacetic Ether.—L. Bouveault and A. Bongert.—M. Scholl prepared, amongst the highest products obtained by the action of silver nitrate on ethyl bromacetate, a liquid whose boiling-point is close to that of the substance the authors obtained during the nitration of acetylacetic ether. The two substances possess the same composition and the same molecular weight. The authors' first idea was to conclude the identity of these two substances, but their present research proves them to be distinct isomers.

A Method of Synthesis of Acetylenic Aldehydes.—Ch. Moureu and R. Delange.—The authors' method of synthesising acetylenic aldehydes is by condensing the formic ethers with acetylenic carbides. Experiment shows that the formic ethers attack the sodium carbides, $R—C\equiv CNa$, with energy, and that the final action of water on the crude product of reaction causes the formation of the acetylenic aldehydes, $R—C\equiv C—CHO$. The operation should be performed at a low temperature (about 0°).

MISCELLANEOUS.

Action of Contact on Secondary and Tertiary Alcohols.—A. Trillat.—The author's experiments show that the action of a platinum spiral is manifested not only on primary alcohols, but also on secondary and tertiary alcohols, with formation either of ketones alone or of ketones and formaldehyde. In all these cases the heat given out by the chemical reaction is sufficient to maintain the platinum spiral in a state of incandescence.—*Comptes Rendus*, cxxxii., No. 24.

Action of Sulphuretted Hydrogen on Acetylacetone.—F. Leteur.—If acetylacetone or its aqueous solution is submitted to a current of sulphuretted hydrogen, no perceptible action takes place; this gas does not act well on the solution in acetic acid solution, even in presence of fused sodium acetate, but if a solution of 20 grms. of acetylacetone in 100 c.c. of strong hydrochloric acid is submitted to the same treatment, at the end of some hours needle-shaped flakes are deposited. At the end of about twenty hours the action apparently terminates, and an abundant crystalline deposit is obtained, which on examination is found to have the formula $(C_5H_8S_2)_2$, and is a diamer of the pentanedithione-2.4.—*Comptes Rendus*, cxxxiii., No. 1.

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1901–2.

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THE CHEMICAL NEWS.

Vol. LXXXIV., No. 2176

ON THE MIXED ESTERS OF CELLULOSE, AND THE RELATIONSHIP OF CELLULOSE TO NITRATING ACIDS (HNO_3—H_2SO_4).*

By C. F. CROSS, E. J. BEVAN, and R. L. JENKS.

We have recently investigated a number of mixed esters of the celluloses and lignocelluloses, more especially the aceto-benzoates and nitrobenzoylnitrates, the results of our investigations having been published elsewhere (Cross and Bevan, "Researches on Cellulose, 1895—1900," Longmans, London, 1901). These mixed esters have been produced for the most part by the successive action of the respective esterifying reagents, the most convenient procedure being to fix first the benzoyl groups upon the cellulose, and to treat the resulting benzoates with acetic anhydride, or for preparing the mixed nitrates, with the usual nitrating mixtures. From the study of the quantitative relationships of these derivatives we have been able to throw some further light on the functions of the OH groups of the celluloses, and from a closer investigation of the reactions we are able to conclude that cellulose in the presence of a mixture of negative radicals under esterifying conditions will combine simultaneously with two or more according to the usual laws governing such reactions.

Without entering into a full discussion of this complicated problem, which we reserve until our investigations are more complete, we wish to deal with the specific case of the formation of the nitric esters by the usual method of treating the fibrous celluloses with a mixture of nitric and sulphuric acids. The function of the latter acid has invariably been assumed to be the indirect one of combining with the water liberated in the reaction between cellulose and the nitric acid; and this general conclusion from the literature of the subject is expressly adopted in the latest investigations of the reaction (Lunge and Bebie, "Beitrage zur Kenntniss der Nitrocellulose," *Ztschr. Angew. Chem.*, 1901, Heft 20).

From our investigations we were led to the conclusion that it was *à priori* improbable that sulphuric acid should play this inert *rôle* in relation to the cellulose, and we have now positive proof that it takes a direct part in the reaction. There are two ways in which the function of combining directly with the cellulose OH-groups may be exerted:—(1). A cellulose sulphuric ester may be formed and immediately decomposed, the NO_3 residue taking the place of the SO_4H residue at first fixed. In this case no evidence of such action would be furnished by the properties or composition of the product. (2). There may be produced as the first product of the joint action of the acids a mixed nitric-sulphuric ester of sufficient stability to persist in the acid mixture, and to withstand the subsequent action of water. In this case the fixation of sulphuric residues will be proved by a simple analysis of the products.

It is this second and more important case which we are able to establish by the following experimental proof. A complete diagnosis of the former will require more extended investigation. Positive evidence, however, is to hand as to the influence of H_2SO_4 in relatively minute proportion.

Samples of selected American cotton were nitrated with a mixture of acids in the usual proportion $\frac{HNO_3}{H_2SO_4} = 1/3$ by weight, the proportion of water alone being varied.

* A Paper communicated to the *Ber. Deuts. Chem. Ges.*, July 4, 1901.

Series 1. The action was continued for one hour at 16° C., the products then washed and exhaustively purified by treatment with boiling water until the wash waters were entirely free from acid products. This required ten to fifteen hours' boiling, the wash water being changed every forty-five minutes. The nitrates were dried and weighed to determine yield, and afterwards destructively oxidised for the estimation of H_2SO_4.

H_2O per cent.	Nitrating acid, H_2SO_4/HNO_3.	Yield.		Per cent H_2SO_4 combined with cellulose in product.
10·14	3/1	171·3		0·00
2·3	3/1	170·6		0·23
0·0	3/1	122·25	*a*	0·83
			b	1·00
0·0	3/1	135·0		1·35

These numbers establish the fixation of the sulphuric residue in combination with the cellulose, the quantity increasing as the acid mixture approaches to the condition of pure "monohydrate."

On the basis of incidental observations we now aimed at an increased fixation of sulphuric acid in the products by reducing the duration of exposure to the acid mixture from sixty to seven minutes. The conditions of purification of the products were also changed, the nitrates being exhaustively washed with cold distilled water, each successive quantity of water being titrated to determine the rate of elimination of the acids. When wash water and nitrate were neutral in reaction the latter was dried off to determine yield, and then destructively oxidised for the determination of H_2SO_4.

Two series of experiments were made—(*a*) with bleached cotton, (*b*) with unbleached. In order to refer the numbers for H_2SO_4 to a uniform basis they are calculated to the weight of the original cotton taken for nitration.

H_2O per cent.	Nitrating acid, H_2SO_4/HNO_3.	Yield of nitrate.	H_2SO_4 fixed. Per cent of product.	H_2SO_4 fixed. Per cent of original cellulose.
		(a) *Bleached Cotton.*		
10 13	3/1	152·7	2·56	3·91
2·30	3/1	162·2	2·52	4 06
0·0	3/1	134·4	4·62	6·21
		(b) *Unbleached Cotton.*		
10·13	3/1	171·55	2·59	4·17
2·3	3/1	163·3	1·87	2·86
0·0	3/1	132·6	1·52	1·89

It is evident that the H_2SO_4 combined is easily eliminated from the nitrates prepared under the ordinary conditions with a somewhat diluted acid mixture, *i.e.*, the sulphuric ester groups are hydrolysed by the ordinary purification process of boiling with water, &c. We also find that the ester groups in question are eliminated by treatment with diluted acetone containing sufficient water to prevent the ordinary solvent action of the acetone upon the nitric esters (Luck and Cross, *Journ. Soc. Chem. Ind.*, 1900, 642). By this treatment we hope to effect a separation of the particular mixed esters in question.

As previously noted, this investigation of the nitrates is only a special case in a systematic enquiry into the relationship of the celluloses to the several negative radicals with which it was previously known to form well-defined compounds, viz., the nitrates, benzoates, acetates, and sulphates.

We make a separate preliminary communication on this case in view of the special interest attaching to the nitrates, and as a direct contribution to the practical question of the causes of instability of the nitrates.

We have pleasure in acknowledging the co-operation of our friend Dr. R. Messel in this scheme of research.

Addendum, *July* 31, 1901.—Since the date of writing the above preliminary communication the experimental evidence has accumulated. The empirical fact of the fixation of sulphuric acid in combination with the cellu-

lose had been carefully separated from all possible errors of analysis, or of conditions of purification of the products. The later investigations have been extended to the conditions of breaking down—by hydrolysis—and of fractionation of the products by graduated solvent actions, with a view to eliminate the mixed ester product assumed to be formed, in the first case, in the form of products of decomposition, and, in the second, as an undecomposed cellulose derivative. It is in these directions that the evidence continues to accumulate that a mixed cellulose nitro-sulphuric ester is formed under certain regulated conditions of treatment with the mixed acids, and that in all cases where cellulose is in presence of both nitric and sulphuric acids, a positive combining function of the latter has to be reckoned with.

4, New Court, W.C., and
89, Bartholomew Close, London, E.C.,
July 1, 1901.

THE ASSAYING OF COMPLEX GOLD ORES.*

By ERNEST A. SMITH, Assoc.R.S.M., F.C.S.,
late Assistant Instructor in Assaying, Royal School of Mines, London.

The advances which have been made in recent years in the metallurgical processes for the successful treatment of complex auriferous ores have led to the adoption of special methods of assay for this class of material.

In this paper the author deals with the principal methods which are used for estimating the precious metals in complex ores.

The expression, "complex ores," includes those ores in which the gold is associated with gangues of basic oxides, such as ferric oxide, alumina, lime, &c., and with metallic sulphides and sulph-arsenides, such as iron and copper pyrites, arsenical iron pyrites, sulphides of antimony and of bismuth, zinc blende, and galena. Those ores are also included in which the gold exists in chemical combination with another substance, as with tellurium in the minerals graphic tellurium (sylvanite), calaverite, and foliated or black tellurium (nagyagite), a class of ores which has attracted considerable attention within recent years.

Many text-books on assaying give universal mixtures for the assay of all classes of complex auriferous ores, but it is obvious that, if reliable results are to be obtained, complex ores must be assayed on scientific principles, each ore being treated with the fluxes and reagents best suited to its composition.

As the selection of the fluxes and the quantity of each to be employed is dependent upon the richness of the ore, the nature of its gangue, and the presence or absence of compounds of the base metals, it is impossible to give definite charges to meet the requirements of all classes of ore; the best method to be used in each particular case must therefore necessarily be left to the judgment and experience of the assayer. The chief fluxes used in the assay of gold ores are sodium carbonate, which is a flux for silica and silicates, and borax, which acts as a flux for lime, oxide of iron, and other bases. The relative quantity of each of these fluxes must be varied according to the nature of the material to be assayed; a mixture of equal weights usually answers very well. One and a half parts of sodium carbonate are required to satisfactorily flux one part of silica.

Powdered sand or glass may be used with advantage as a partial or complete substitute for borax, especially with materials rich in metallic oxides.

Litharge is a powerful base, and is sometimes used to flux siliceous materials. It is a very useful flux under certain conditions, as it forms fusible compounds with oxides that are infusible alone, and on this account there is sometimes an advantage in having an excess of lead oxide in the slag. This is particularly the case when oxides of copper are present in the material to be assayed. Red-lead is frequently used instead of litharge.

Lead oxides are used chiefly as a source for lead for collecting the gold and silver, but they are occasionally employed as oxidising agents to oxidise sulphur, arsenic, antimony, &c. Red-lead is used with advantage for pyritic gold ores where an oxidising action is required in the fusion, while litharge, which contains less oxygen, is well adapted for ores with much quartz, or where the conditions of the fusion are reducing.

Carbon, chiefly as charcoal, is largely employed as a reducing agent. Flour or argol may be substituted for charcoal where the latter is not to be conveniently obtained. Two grms. of flour or 5 grms. of argol equal 1 grm. of charcoal in reducing power.

Nitre is a powerful oxidising agent, and is used with advantage to oxidise compounds of the base metals present in certain complex ores which cannot be conveniently oxidised with hot air. For materials containing sulphates of baryta or lime, or phosphate of lime, fluor-spar may be added with advantage, as it helps to increase the fluidity of the charge.

The amount of flux required is judged in the first place from the appearance of the ore, and is subsequently modified according to the result of the fusion. It is well in this connection to bear in mind the general principle that for basic material an acid flux is needed, and for an acid or siliceous gangue a basic flux. Three parts of flux are usually quite sufficient to yield a fluid slag with one part of ore, but if it be found that this is not sufficient the remedy lies in using a different flux rather than in taking a larger quantity.

All samples of complex ores should be reduced to fine powder and passed through a sieve of 80 holes to the linear inch. The question of fine powdering is of much importance in dealing with complex ores.

The assay of gold ores is in most cases conducted by the fusion or crucible process, but occasionally the scorification process is used.

Wet methods are scarcely applicable owing to the extremely small proportion which the gold bears to the worthless gangue with which it is accompanied. In exceptional cases a combined wet and dry process may be employed with advantage.

The crucible methods of assaying complex ores vary somewhat according to the nature of the substances to be operated upon, and will for convenience be described under the following heads:—

Basic oxidised ores.
Pyritic ores.
Telluride ores.
Bismuth ores

Basic Oxidised Ores.

The chief ores which come under this head are those consisting mainly of limonite or hydrated oxide of iron. Ores containing magnetite, calcite, and dolomite, and those which are largely composed of the sub-crystalline, slaty, or schistose rocks, may also be included under this head.

One of the chief considerations in the assay of materials consisting chiefly of ferric oxide (Fe_2O_3) is the reduction of the higher oxide to the ferrous state (FeO), in which state alone it unites with silica to form a readily fusible compound. Ferric oxide being infusible, its presence in the slag tends to stiffen it and render it pasty. Experience has shown that the separation of the gold in the ore is more or less incomplete when much ferric oxide is present in the slag. The reduction of the iron to the state of the lower oxide is effected by the addition of charcoal powder or other reducing agent to the charge, the quantity added being in excess of that needed to provide the lead for collecting the gold. With ores consisting mainly of ferric oxide the quantity of charcoal powder required will be

* Abstract of Paper read before Institution of Mining and Metallurgy, May 15, 1901.

about one-twelfth part of the weight of ore taken for assay; the exact amount needed for any particular ore must, however, be left to the experience of the assayer.

The proportion of alkaline flux required for ores containing much iron oxide is comparatively small, as the ferrous oxide formed during the fusion combines with silica, with the production of ferrous silicate, which is easily fusible. The addition of alkaline fluxes results in the formation of double silicates, which greatly increase the fusibility of the slag. It may be pointed out, however, that the addition of proportionately large quantities of alkaline flux to ores containing oxides (such as iron and manganese), which form easily fusible silicates, is a decided disadvantage, inasmuch as they cause the charge to melt too rapidly, and thus prevent the complete collection of the precious metals. As a general rule the proportion of sodium carbonate should be diminished as the quantity of metallic oxides in the ore becomes greater, while the proportion of borax, lead oxide, and charcoal should be increased.

Sodium carbonate may be altogether omitted for ores practically free from siliceous material, and the deficiency of silica allowed for by the addition of fine sand or powdered glass, otherwise excessive corrosion of the crucible will result.

For ores ranging from moderately basic (with about 30 per cent of ferric oxide), to very basic, the following proportions may be taken :—

	Moderately basic. Grms.	Very basic. Grms.
Ore	50	50
Litharge	40	50
Charcoal powder	2·5	4 to 6
Borax	20	30
Sodium carbonate	30	10 to 15
Sand or glass	Nil	10 to 20

The charge should be covered with a layer of powdered salt to prevent the oxidation of the slag.

The lead button resulting from the fusion should weigh from 25 to 35 grms., and with ores practically free from iron oxide 2 grms. of charcoal are sufficient to produce this result; but as the proportion of iron oxide increases, the amount of carbon must also be increased for the reason stated above. For ores consisting mainly of iron oxide, 4 grms. of charcoal are usually sufficient to produce the desired weight of lead, but in exceptional cases a larger quantity may be required. A sample of gold ore, practically pure hæmatite, assayed by the author, required 6 grms. of charcoal; another sample which was mainly micaceous hæmatite also required this amount. In both cases 20 grms. of fine sand were used, the quantities of the other fluxes being the same as those given above. If more than the desired weight of lead is obtained, it should be reduced to convenient size by scorification, since less loss of the precious metals is incurred by scorifying lead than by cupelling it.

Peroxide of manganese is not commonly associated with gold ores, and if present it is usually in small proportion only. It requires about twice the amount of charcoal for its reduction to the lower oxide as compared with iron oxide; due allowance must therefore be made in the amount of charcoal added when large proportions of peroxide of manganese are present. The quantity of litharge should be slightly increased for ores containing small quantities of copper or antimony oxides, the amount required being usually from 60 to 70 grms. for a charge of 50 grms. of ore. The excess of lead oxide passes into the slag, and carries the copper and antimony with it, thus preventing the production of cupriferous or antimonial lead.

For ores consisting mainly of earthy bases—such as lime, alumina, &c., or of zinc oxide—the quantity of alkaline flux is advantageously increased to 60 grms. A piece of hoop iron should be added to the charge for ores containing small quantities or iron pyrites, for the reasons stated in the section dealing with pyritic ores.

The fusion of the charge is an operation which too frequently receives but scant attention at the hands of the assayer, but it may be pointed out that the success or failure in collecting all the gold in the sample is to a large extent dependent on the care bestowed on the fusion. This remark is specially applicable to ores containing much ferric oxide. The crucible is placed in the furnace at a red heat, and the temperature gradually raised to full redness. The temperature should not be raised too rapidly at first; a dull red heat is maintained for about ten minutes to ensure the complete fritting of the charge before actual fusion takes place; this is a point which is frequently neglected. Rapid increase of temperature will cause a quick evolution of carbonic acid from the decomposition of the alkaline carbonate, and a corresponding loss from projection. When effervescence has ceased, and the contents of the crucible have become thoroughly liquid and tranquil, it is removed from the furnace, and its contents poured into an ingot mould. The time which elapses from the introduction of the charged crucible into the furnace to the final pouring usually varies from thirty to forty minutes. Prolonged or excessive heating should be avoided, as it tends to thicken the slags. The button of lead should weigh from 25 to 35 grms., and the amount of charcoal added to the charge must be altered as may be necessary to secure this end. The lead is cupelled, and the resulting gold-silver button weighed and parted in dilute nitric acid in the usual way.

It is not usually necessary to clean the slags from the assay of gold ores, but when the ores are very rich and contain large quantities of the oxides of iron or of manganese it is very advisable to do so. For this purpose the slag is collected, roughly powdered, and "cleaned" by mixing with the following charge :—

Litharge	30 grms.
Charcoal powder	1·5 „
Sodium carbonate	10 „

The charge is placed in the crucible previously used for the fusion and kept in a molten state from ten to fifteen minutes. If the fused product is thick and pasty, a small quantity of borax may be added with advantage. The button of lead obtained in this fusion is either cupelled by itself or with the assay button previously obtained.

Pyritic Ores.

Native gold, *in situ*, is most frequently met with in quartz veins intersecting metamorphic rocks, and is almost invariably associated with iron pyrites and other metallic sulphides and sulph-arsenides, which are also technically known as "sulphurets."

Under these conditions it is not surprising that the larger proportion of complex ores with which the assayer has to deal comes under the somewhat vague title of "pyritic ores." In order to facilitate the description of the various processes adopted for the assay of ores of this class, the following subdivision will be made :—

Pyritic ores (mainly iron pyrites).
Arsenical ores.
Antimonial ores.
Cupriferous ores.
Ores with galena and zinc blende.

The author is well aware that in pyritic ores it is more usual to find several sulphides associated with the ore than to find one sulphide only, and due consideration will be given to this fact in dealing with the different sulphides enumerated.

Pyritic Ores (mainly Iron Pyrites).—The assay processes for the treatment of pyritic ores are chiefly based on the various methods employed for the removal of the sulphur.

The elimination of the sulphur is necessary, otherwise it will pass into the lead, making it more or less brittle, or the lead will be accompanied by a layer of regulus or artificial sulphide.

The methods for the removal of the sulphur may be summarised as follows:—

(*a*) Oxidation by roasting.
(*b*) ,, with nitre.
(*c*) ,, with lead oxide.
(*d*) Desulphurisation with metallic iron.

Method (*a*).—The elimination of the sulphur by an oxidising roasting of the ore previous to fusion is undoubtedly the most satisfactory method of dealing with pyritic ores in which iron pyrites or mispickel predominates.

Many assayers, however, hesitate to roast their ores, on the assumption that gold is lost during the process. Although this may be true when proper precautions are not taken, it may be remarked that the loss of gold experienced is, in many cases, more probably due to want of care in conducting the operation, or to the retention of gold in the slag owing to improper adjustment of the charcoal in the charge for fusing the roasted ore.

The quantity of ore to be used for assay should be weighed out before roasting. The roasting is most conveniently effected in shallow clay dishes in a muffle or in the crucible in which the fusion is subsequently performed. The temperature at which the roasting is started is not a matter of indifference, as it is during the first few minutes of the operation that the formation of lumps is most to be feared. A dull red heat should be employed at first, and the ore frequently stirred, though not violently, to expose fresh surfaces to the air, and to prevent fritting. The employment of too high a temperature at the outset, or neglect in stirring, will cause partial fusion of the sulphides, and the formation of matter troublesome to roast. The ore is maintained at dull redness until all blue flame has ceased and no incandescent particles are visible on stirring, after which the temperature is raised to full redness to decompose sulphates.

A high temperature at the outset facilitates the formation of arseniates and antimoniates, and will frequently cause a mechanical loss of gold and silver owing to the rapid disengagement of the volatile constituents of the ore, the vapours of which tend to carry off the precious metals. The mechanical loss during roasting may be considerable when proper precautions are not taken. The chief causes of loss are excessive agitation of the ore and decrepitation of the pyritic material, due in many cases to the coarseness of the powdered sample.

The roasting, which occupies from thirty to sixty minutes for 50 grms. of ore, is complete when the ore remains of a uniform colour on stirring, and no more fumes of sulphurous acid can be perceived. Excessive or prolonged heating of the ore should be avoided, as it tends to produce magnetic oxide ($3Fe_2O_3=2Fe_3O_4+O$), which is undesirable, since this oxide is more difficult to flux than ferric oxide.

Arseniates and antimoniates are stable at high temperatures, and will cause loss of precious metals in the subsequent fusion of the roasted material unless previously decomposed. The reduction of these compounds and also of sulphates is effected by mixing a small quantity of charcoal or anthracite powder with the ore after it has been completely oxidised, and roasting again for a short time at a bright red heat. Arseniate of iron is readily decomposed when heated with charcoal powder, and practically the whole of the arsenic eliminated, but the reducing action of charcoal on arseniate of copper is very small, only a slight elimination of arsenic taking place. Hence it is very necessary in the case of arsenical ores, especially when copper is present, to effect the elimination of the arsenic as completely as possible during the early stage of the roasting. Antimoniates are also decomposed by charcoal, but less easily than most arseniates, the antimony being eliminated to a large extent on re-roasting.

Ores containing tellurium or large quantities of antimony or of lead should not be roasted, ores of this description being more satisfactorily treated by special methods.

The fusion of the roasted ore is effected in the same manner as described for ores with much metallic oxides, to which class they belong.

Experience will frequently enable the adjustment of the charcoal to be made from the colour of the roasted ore.

(To be continued).

A NEW INDICATOR FOR USE IN DETERMINING TOTAL ACIDITY OF WINES.*

By E. G. RUNYAN.

In maintaining a chemical control of a beet-sugar house, it is often necessary to determine by some rapid method the excess of alkali in the juices, syrups, and massecuites. The usual method is to titrate the material with a standard acid solution. As these products vary in colour from a light amber to a dark brown, or nearly black, the ordinary indicators often give very unsatisfactory results, or fail entirely, on account of the difficulty of noting the end reaction.

To meet this difficulty, a French chemist, L. Lachaux, in 1892, proposed a mixture of corallin and malachite green† prepared as follows:—

Three and one-tenth grms. of corallin or commercial rosolic acid are dissolved in 150 c.c. of 90 per cent alcohol, neutralised and mixed with 0·5 grm. malachite green dissolved in 150 c.c. of alcohol. With this mixture alkalis give a purple colour, which is changed to a green by acids.

Malachite green dissolves in alcohol, yielding a greenish blue solution, which possesses no value as an indicator by itself, but when mixed with corallin it blends with the colours of that indicator and renders the end reaction more distinct. As only the corallin in this mixture acts as an indicator, it follows that this corallin-malachite mixture can be used in titrating only those acids and bases which give a distinct end reaction with corallin alone.

Recently I had occasion to make use of this indicator in determining the amount of alkali in a highly coloured sample of beet molasses, and obtained very satisfactory results. It occurred to me at once that this indicator might be used advantageously in determining the total acidity of such highly coloured products as wines, vinegars, and ciders, since, as is well known, the present methods are far from satisfactory in the case of red or highly coloured wines. The method adopted by the Association of Official Agricultural Chemists for the determination of total acidity in wines is as follows:—

"Transfer 10 c.c. of the sample to a beaker, and in case of white wines add about 10 drops of a neutral litmus solution, and titrate with decinormal sodium hydroxide solution until the red colour changes to violet. In case of red wines, continue adding a few drops at a time of alkali solution, until a drop of the mixture placed on delicate red litmus-paper shows an alkaline reaction."

Another method in use by some chemists is to dilute 10 c.c. of the wine to about 300 c.c. with boiling distilled water, heat the mixture to boiling for a moment to expel carbon dioxide, add a few drops of phenolphthalein solution, and titrate with decinormal sodium hydroxide solution.

Any one who has ever tried either one of the above methods with a claret or other red wine will, I think, agree with me that the determination of the exact point of neutrality is very uncertain.

To test the corallin-malachite indicator in comparison with phenolphthalein and litmus, three samples of wine were procured—(1) a claret, as a type of red wine; (2) a Rhine wine for the white type; and (3) a sherry for the

* Read before the Washington Section of the American Chemical Society, March 14, 1901. From the *Journal of the American Chemical Society*, xxiii., No. 6.

† The zinc-double-chloride of tetramethyldi-*p*-amidotriphenyl-carbinol, $(C_{23}H_{22}N_2Cl_2)_2+2ZnCl_2+2H_2O$.

medium colour. In this experiment the following method was employed:—

Transfer 10 c.c. of the sample to a beaker, dilute with about 300 c.c. of boiling distilled water, heat the mixture to boiling for a moment to expel all carbon dioxide, cool to about 75°, add 10 drops of the corallin-malachite solution, then add an excess of decinormal sodium hydroxide solution, indicated by a purple colour, titrate the excess of alkali with decinormal acid solution, adding the acid solution slowly until the appearance of a distinct green colour. The change in colour is best observed by transmitted light. A trial showed that that it was easier to detect the transition from the alkali to the acid side than the reverse.

With phenolphthalein and litmus, slightly more of the indicator was used, and the decinormal soda solution added slowly to the point of neutrality as near as that could be determined. The results are expressed as usual in terms of tartaric acid, 1 c.c. decinormal sodium hydroxide solution = 0·0075 grm. tartaric acid. The following are the results obtained:—

Grms. Tartaric Acid in 100 c.c. of Wine.

Wine.	Corallin-Malachite.	Phenolphthalein.	Litmus.
1. *Claret*	0·840	0·995	0·890
	0·870	0·980	0·920
	0·870	0·980	—
	0·880	—	—
	0·875	—	—
Average ..	0·867	0·985	0·905
2. *Rhine Wine* ..	0·705	0·730	0·730
	0·710	0·725	0·720
	0·705	0·730	0·725
	0·695	0·735	—
	0·705	—	—
	0·705	—	—
	0·695	—	—
Average ..	0·703	0·730	0·725
3. *Sherry* ..	0·450	0·490	0·475
	0·430	0·475	0·460
	0·440	0·475	0·460
	0·445	0·475	0·460
	0·435	—	—
	0·430	—	—
Average ..	0·438	4·479	0·464

The results obtained with corallin-malachite are invariably lower than those obtained with the other indicators, but this was to be expected when we consider that with the corallin-malachite the titration was made toward the acid reaction, and with the other indicators it was made toward the alkali side.

The greatest difference appears in the results on the claret or red wine, where in case of phenolphthalein and litmus it was necessary to add a decided excess of alkali before the change of colour could be detected. I am inclined, therefore, to believe that the results with corallin-malachite more nearly represent the true figure for total acidity of this sample.

To test the sensitiveness of the corallin-malachite, five drops of the mixture were added to 100 c.c. of distilled water, when 0·1 c.c. of 0·01 normal hydrochloric acid solution or 0·01 normal sodium hydroxide solution was sufficient to give a distinct acid or alkali reaction.

In the presence of other colouring matters, slightly more of the standard solutions was required.

In consideration of the encouraging results obtained with this corallin-malachite mixture in my hands, I feel justified in recommending this indicator to the attention of chemists engaged in the analysis of wines, vinegars, ciders, and similar products.

ON THE METEORIC STONES WHICH FELL NEAR ZOMBA, BRITISH CENTRAL AFRICA, ON JANUARY 25TH, 1899. WITH NOTES ON THE CHEMICAL ANALYSIS OF SUCH BODIES.*

By L. FLETCHER, M.A., F.G.S.,
Keeper of Minerals in the British Museum.

(Continued from p. 45).

Section II.—Calculations.

Interpretation of the Analytical Results.

Atomic Weights.

21. The atomic weights used in the following calculations are those recommended by Professor F. W. Clarke, in the "Seventh Annual Report of the Committee on Atomic Weights (*Journ. Amer. Chem. Soc.*, 1900, xxii., 70; Chem. News, lxxxi., 146), namely:—

Al	26·9	Mg	24·1
Ba	136·4	Mn	54·6
Ca	39·8	Na	22·88
Cl	35·18	Ni	58·25
Co	58·55	O	15·88
Cr	51·7	P	30·75
Cu	63·1	Pt	193·4
Fe	55·6	S	31·83
H	1	Si	28·2
K	38·82		

It is convenient to make the calculations in the following order.

Undecomposed Material.

22. *Alkalis.*—K_2PtCl_6 0·0079 (§ 16) corresponds to KCl 0·0024; 0·0025, adherent to the filter and ignited, if taken as Pt.2KCl, corresponds to KCl 0·0019; making altogether KCl 0·0035. From the blank experiment (§ 8), K_2PtCl_6 0·0056 and Pt.2KCl 0·0012 correspond respectively to KCl 0·0017 and KCl 0·0005; making in all 0·0022; as the direct weight of the chlorides was only 0·0021, the whole 0·0021 must have been potassium chloride. The potassium chloride due to the silicate is thus 0·0014. The mixed chlorides due to the silicate weigh 0·0183 (§ 16)—0·0021 (§ 8) or 0·0162; hence the NaCl due to the silicate is 0·0148.

These amounts of NaCl and KCl correspond respectively to Na_2O 0·0079 and K_2O 0·0009 for 0·4994 of undecomposed material, and to Na_2O 1·58, K_2O 0·18 per cent; no stress can be laid on the number for K_2O.

As the undecomposed material had been boiled three times, each time for five minutes, in a strong sodic solution, it is not inconceivable that soda might have been introduced into its composition. But the residue had been subjected to a very long continued washing to secure the complete removal of soluble matter; further, there is already a certain amount of sodium in the mixed silicates before the digestion with sodic solution (§ 5, § 8), and a consideration of the weights of the soda in the mixed silicates and the undecomposed material suggests that the sodium is an original constituent of the latter.

23. 0·1201 (§ 15) of mixed oxides consists of Cr_2O_3 0·0054, Al_2O_3 0·0333, Fe_2O_3 0·0808, and SiO_2 0·0006; hence 0·1545 of mixed oxides consists of Cr_2O_3 0·0070, Al_2O_3 0·0428, Fe_2O_3 0·1039 (and SiO_2 0·0008, due to the action on the glass).

Cr_2O_3 0·0070 must have been originally present as chromite ($FeO.Cr_2O_3$) and requires FeO 0·0033; chromite 0·0103 has thus been decomposed; further, undecomposed chromite 0·0027 was admixed with the main silica. The total chromite was therefore 0·0130.

Fe_2O_3 0·1039 corresponds to FeO 0·0935; of this, 0·0033 is due to chromite, leaving 0·0902 for the silicate.

MnS 0·0042 corresponds to MnO 0·0034.

Deducting 0·0054 (§ 20) from the weight obtained for the $Mg_2P_2O_7$ 0·5384, the pure $Mg_2P_2O_7$ is 0·5330, corresponding to MgO 0·1930.

* From the *Mineralogical Magazine*, vol. xiii., No. 59, 1901.

For 0·8981 of undecomposed material (§ 15), Na_2O is 0·0141 and K_2O 0·0016 (§ 22).

Hence we have the following numbers :—

		Zomba. Percentages for silicate.	Zomba. Oxygen.		Linn County. Percentages for silicate.
Chromite .	0·0130	—	—		—
SiO_2 . ..	0·5029	56·83	30·10		55·08
FeO.. ..	0·0902	10·19	2·26	12·22	13·58
MnO . ..	0·0034	0·39	0·09		
MgO . ..	0·1930	21·81	8·68		22·70
CaO . ..	0·0369	4·17	1·19		2·85
Al_2O_3 ..	0·0428	4·84	2·27		4·86
K_2O . ..	0·0016	0·18	0·03	0·44	trace
Na_2O ..	0·0141	1·59	0·41		0·93
Total ..	0·8979	100·00			100·00
Wt. taken.	0·8981				

The percentage composition of the silicate approaches very closely to the corresponding silicate in the Linn County meteorite as analysed by Rammelsberg (*Monatsb. Ak. Wiss. Berlin*, 1870, p. 458).

24. The undecomposed material being insoluble in water, the alkalis must be present as constituents of an insoluble compound, presumably felspar; the presence of the latter is further suggested by the fact that the dyad constituents are insufficient to form an aluminous pyroxene with the alumina and silica.

The CaO cannot be wholly present as a constituent of lime-felspar ($CaO.Al_2O_3.2SiO_2$); for in such case the oxygen of the Al_2O_3 must have been 3·57 instead of 2·27, without the alumina required for the soda-felspar being taken into account.

Hence it is reasonable to assume :—

1. That all the alumina is due to felspar (an admixture of albite and anorthite).
2. That all the alkali is due to felspar (albite).
3. That the excess of lime above that required to form felspar is a constituent of the remaining silicate (enstatite).

With these assumptions the following numbers may be obtained :—

The oxygen of $(Na,K)_2O$ being 0·44, that of the Al_2O_3 and SiO_2 forming albite ($Na_2O.Al_2O_3.6SiO_2$) will be respectively 1·32 and 5·28. The total oxygen of the Al_2O_3 being 2·27, there is left 0·95 for the oxygen of the Al_2O_3 forming anorthite ($CaO.Al_2O_3.2SiO_2$); the oxygen of the corresponding CaO and SiO_2 will thus be respectively 0·32 and 1·28.

We therefore have the following distribution of the oxygen :—

	Total oxygen.	Oxygen of— Enstatite.	Albite.	Anorthite.
SiO_2	30·10	23·54	5·28	1·28
FeO	2·26	2·26	—	—
MnO	0·09	0·09	—	—
MgO	8·68	8·68	—	—
CaO	1·19	0·87	—	0·32
Al_2O_3	2·27	—	1·32	0·95
K_2O .. .. Na_2O	0·44	—	0·44	—

The total oxygen of the bases of the enstatite, namely, 11·9, is slightly more than half that of the silica (23·54). On the other hand, the original constituents of the meteorite have been digested first with hydrochloric acid and then with sodic solution; the latter, while removing the free silica, would be expected to act to some extent on the silicates which resisted the acid, and to carry away the resultant silica, alumina, and lime, leaving the corresponding oxides of iron and magnesia from the decomposed enstatite as part of the final residue.

25. The above distribution of oxygen corresponds to the following composition for the silicates themselves :—

	Enstatite.	Felspar. Albite.	Anorthite.	Total.
SiO_2	44·44	9·97	2·42	56·83
FeO	10·19	—	—	10·19
MnO	0·39	—	—	0·39
MgO	21·81	—	—	21·81
CaO	3·04	—	1·13	4·17
Al_2O_3 ..	—	2·78	2·06	4·84
K_2O	—	0·18	—	0·18
Na_2O ..	—	1·59	—	1·59
		14·52	5·61	
	79·87	20·13		100·00

26. The composition of the above felspar is—

	Percentages.		Calculated for oligoclase (Ab_5An_1).
SiO_2	12·39	61·55	62·1
CaO	1·13	5·61	5·3
Al_2O_3	4·84	24·04	23·9
K_2O	0·18	0·90	8·8
Na_2O	1·59	7·90	8·7
	20·13	100·00	100·0

27. The percentage composition of the above enstatite is—

	Zomba enstatite.	Lodran enstatite.
SiO_2	55·64	55·35
FeO	12·76	12·13
MnO	0·49	—
MgO	27·31	32·85
CaO	3·80	0·58
Al_2O_3	—	0·60
	100·00	101·51

The numbers thus obtained for the Zomba enstatite are very similar to those obtained by Professor Tschermak for the Lodran enstatite; in the latter case the enstatite grains were so coarse that they could be picked out, and a sufficient amount be separated for a special analysis (*Sitzungsb. Ak. Wien*, 1870, Band lxi., Abtheil. 2, p. 465).

28. The mineral composition of the undecomposed material is—

Enstatite	79·87
Oligoclase	20·13
Chromite	1·47
	101·47

	78·71
	19·84
	1·45
	100·00

(To be continued).

CONTRIBUTIONS TO THE SCIENCE OF THE NITROCELLULOSES.*

By G. LUNGE and J. BEBIE.

(Continued from p. 56).

B. *Influence of Sulphuric Acid upon the Process of Nitration.*

As already remarked, nothing above decanitrocellulose can be obtained with nitric acid alone. A higher degree of nitration can only be reached by adding a substance with an affinity for water, and of such sulphuric acid is the simplest to use. Hence, while the latter is essential to the production of gun-cotton, nitric acid alone is sufficient for collodion cotton. Yet, industrially, the lower stages of nitration are also always produced with a mixture of the two acids, on economical grounds, for in this manner there is a saving in nitric acid as well as an increase in the speed of reaction. The proportion of nitric acid to

* *Zeitschrift fur Angewandte Chemie*, 1901, Heft 20.

sulphuric varies very much; in the prescriptions printed in books it varies from 1 : 1 to 1 : 6. The results obtained with the proportion 1 : 1 are in the tables given hitherto, especially No. III. In the following research the proportion was varied and nitration conducted at different degrees of dilution.

In order to be able to state the results directly as the action of the sulphuric acid, the ratio of the cellulose to the nitration mixture was so chosen that the ratio of the nitric acid contained in the latter to the cellulose was the same as in the first series of researches. The difference in the results must then be regarded as the action of the sulphuric acid. There were about 30 parts of nitric acid to 1 of cellulose.

The results obtained with mixtures of nitric and sulphuric acid in the ratio 1 : 3 are shown in the following table :—

Expt.	C.c. NO per 1 grm.	Per-centage N.	Solubility in ether-alcohol.	Increase.	Ratio cellulose : HNO_3.
1.	210·69	13·21	3·20	174	1 : 30
2.	198·10	12·42	98·70	160	
3.	186·90	11·72	99·28	157	
4.	174·81	10·96	99·50	148	
5.	187·30	11·74	99·98	159	1 : 12
6.	173·83	10·90	99·20	149	

The nitration mixtures had the following composition after the analyses :—

Expt.	1.	2.	3.	4.	5.	6.
H_2SO_4 ..	62·18	61·53	60·30	58·88	59·77	58·34
HNO_3 ..	21·91	20·02	19·71	19·60	20·94	20·62
H_2O ..	15·91	18·45	19·99	21·52	19·29	21·04

The product obtained in Expt. 2 corresponded to the pyrocollodion of Mendeleeff in nitrogen content and in solubility.

By comparing the results with Table III., we see (by means of a curve) that the rise in the ratio of nitric acid to sulphuric from 1 : 1 to 1 : 3 gives an increase in nitrogen of about 10 c.c. NO. Therefore, with the same amount of water, the ratio 1 : 3 attains to almost a whole stage higher than the ratio 1 : 1, keeping the ratio of cellulose to nitric acid constant. A decrease of the latter from 1 : 30 to 1 : 12 causes a decrease in nitrogen of about 5 c.c. NO.

A few more experiments were carried out with the ratios of nitric to sulphuric acid 1 : 4 and 1 : 5 respectively, the following being the results obtained :—

Expt.	C.c. NO per 1 grm.	Per-centage N.	Increase.	Ratio of HNO_3 to H_2SO_4.	Ratio of cellulose to HNO_3.
1.	192·65	12·08	163	1 : 3·8	1 : 30
2.	179·10	11·23	153		
3.	187·58	11·76	156		1 : 12
4.	175·23	10·99	151		
5.	198·32	12·43	167	1 : 5	1 : 30
6.	185·89	11·66	158		
7.	168·00	10·53	140		1 : 8
8.	149·12	9·35	—		

Composition of the Nitration Mixtures used.

Expt.	1 and 3.	2 and 4.	5.	6.	7	8
H_2SO_4 ..	63·84	62·52	67·60	66·37	64·85	64·11
HNO_3 ..	16·96	16·46	13·66	13·04	14·90	13·62
H_2O ..	19·20	21·02	18·74	20·59	20·25	22·27

The results with the acid ratio 1 : 3·8 are almost identical with those of 1 : 3.

When the quantity of sulphuric acid is five times that that of the nitric acid, there is a rise of the nitrogen content of about 40 c.c. NO, as compared with that of the acid ratio 1 : 3, from which it is evident that the increased action of the sulphuric acid is somewhat limited. It is principally manifested when the ratio rises from 1 : 1 to 1 : 3.

The nitrogen content diminishes rapidly when, in an acid mixture 1 : 5, the ratio of cellulose to nitric acid falls from 1 : 30 to 1 : 8.

All these experiments were carried out at the temperature of the room, and the time of nitration was twenty-four hours. With nitration mixtures of ratios 1 : 3, 1 : 3·8, 1 : 5 respectively, nitrations were conducted at raised temperatures. After two hours' reaction at 35° the same products were obtained as with the above conditions. The nitrogen content was the same, or slightly higher.

According to the results of this section (B), the most important factor in nitration processes is certainly water. In working according to prescription to obtain a certain nitration product, the chief point to observe is that the proper proportion of water is present in the acid mixture. With regard to the amount of sulphuric acid, such accuracy is less necessary, especially with great excess of the acid, as the results are only influenced by this factor to a slighter degree.

(To be continued).

AN IMPROVED METHOD OF PRODUCING ULTRA-VIOLET-SENSITIVE PLATES.*

By V. SCHUMANN.

(Continued from p. 55).

Spectral Characteristics of the Plate.—If an ultra-violet plate and a very slightly sensitive silver bromide gelatin plate are exposed equally to white light it will be seen that the latter receives an impression capable of development in a far shorter time than the former, for the ultra-violet plate is very little sensitive to visible rays. This holds for the greater part of the ultra-violet spectrum. At 231 $\mu\mu$ it begins to yield more than the gelatin plate, giving more intense and sharper images. Further on towards the shorter waves this activity increases to such a visible extent that the distribution of energy and intensity of the field between 220 and 200 $\mu\mu$, the reproduction of which is well known by all experimenters to lack intensity definition, undergo a complete change. All reproductions of this spectral region represent far more the absorption spectrum of the gelatin than the sensibility spectrum of the sensitive portion of the plate. It is the same with the region between 231 $\mu\mu$ and the green part of the spectrum, where intensity and sensibility are both in an opposite sense dependent on the gelatin, which here acts as a sensitising agent, and considerably raises the sensibility of the silver bromide.

It follows from this that all measurements of light intensity, dependent on the density difference of the spectrum image, are only of relative value, and further, that they do not hold for the ordinary gelatin plate, but only for the plate formerly in use. Consequently, plates of different origin may lead to considerable variations. This fact is more important (as is generally accepted) for spectroscopy, which measures the degree of brightness of the different rays according to the degree of blackening of the lines photographed.

The ultra-violet plate can, in consequence of its sensibility, claim higher distinction than any other plate, on the one hand, for rays only to be photographed in vacuo; and on the other hand, for the uniform reproduction of the rest of the spectrum. To what extent the latter is the case may be demonstrated by spectra of the electric aluminium spark, photographed under similar conditions upon an ultra-violet plate and a gelatin dry plate respectively.

A comparison of both shows how fundamentally different are the representations of energy derived from the same source of light, how little adapted is the commercial plate to the photography of the refrangible part of the ultra-violet up to 185 $\mu\mu$, and how little its sensitiveness to light accords with that of pure silver bromide, which, according to earlier researches of mine, reproduces

* *Annalen der Physik*, 1901, vol. v.

uniformly all rays of the spectrum, from the blue portion to the smallest waves. It is further worthy of note that the extremely small quantity of gelatin used usually increases the sensitiveness of the ultra-violet plate. It is only thus possible to obtain soft half-tones in the photograph, which are not indicated by silver bromide alone.

A further advantage of the ultra-violet plate lies in its insensibility towards the diffused light of the photographic apparatus, which renders certain operations with the ordinary plate difficult in the hightest degree. For example, all reproductions of the spectrum beyond 185 $\mu\mu$ become fogged before the image has attained sufficient power, and so completely that only the most active lines remain visible. This fogging is due to the action of the rays that become scattered inside the lenses and prisms, and reach the plate as diffused light. As the diffused light consists principally of less refracted rays, *i.e.*, of rays which act more powerfully than all others on the gelatin plate, fogging is the natural result. So far, it has not been possible, for want of a suitable light-filter, to banish entirely this diffused light from the spectral apparatus, and one has to be content with diminishing it. This is attained without trouble by diminishing the amount of light passing through the slit by shortening the latter (to about $\frac{1}{2}$ m.m.) This is the only way to conduct reproductions of electric discharges above the wave-length 185 $\mu\mu$ to the limit of ultra-violet activity of the ordinary dry plate (182 $\mu\mu$). The ultra-violet plate does not suffer from the diffused light because it is little sensitive to the visible and neighbouring ultra-violet rays. With this, therefore, the length of the slit may be regulated at will without the fear that length of exposure will cause fogging.

(To be continued).

COMPOUNDS OF METHYL SULPHIDE WITH HALIDES OF METALS.*

By FRANCIS C. PHILLIPS.

WHEN methyl sulphide is added to a solution of palladium dichloride a voluminous yellow precipitate is produced, which is apparently flocculent, but upon microscopic examination is seen to consist of very fine indistinct crystals.

If the liquid containing the precipitate is heated, the precipitate re-dissolves, giving a liquid of a bright orange colour. On cooling, this solution deposits orange coloured needle-shaped crystals which may be washed and dried, apparently without change, and are stable in air, and unaffected by light. The crystals are quite soluble in boiling water, but very slightly soluble in the cold.

An analysis of the crystals was made in the following manner:—

A portion of the substance was dissolved in water, and a current of carbon monoxide passed through the solution, which was kept upon a water-bath. Metallic palladium was precipitated. This was filtered through an asbestos filter, previously weighed. After drying, the metal was heated in a stream of hydrogen, and then, without admitting air, dry nitrogen was passed through the tube, and the metal finally allowed to cool in the stream of nitrogen. Experiments demonstrated that the finally divided palladium could be thus easily brought to constant weight. The nitrogen used was prepared from air by the use of alkaline pyrogallate to remove oxygen, and subsequent passage over a heated mixture of copper and copper oxide. The hydrogen chloride in the filtrate from the palladium was neutralised by zinc, and the chlorine then determined volumetrically by silver nitrate solution.

The determination of sulphur presented difficulties. Many experiments were made in attempts to oxidise the sulphur of the compound to sulphuric acid by fusion with various mixtures of alkaline carbonate with nitrate and chlorate, and with sodium peroxide. All these experiments proved fruitless, as in every case a portion of the sulphur was lost by volatilisation. Heating with nitric acid in a sealed tube failed to yield complete oxidation, even at temperatures which involved danger to the tube. The ordinary reagents which might be looked to for the conversion of sulphur into sulphuric acid, are of little use in the case of alkyl sulphides and their compounds. The most feasible method seemed to be by direct combustion in oxygen, and this was attempted in the following manner:—The substance contained in a porcelain boat was placed in a porcelain combustion tube, which was heated to a high temperature in a furnace. The front end of this tube passed through a cork in the neck of a nitrogen flask, containing a solution of sodium hypobromite. To permit of this mode of connection, it was necessary to place the furnace in a strongly inclined position. The products of the combustion passed through a roll of platinum gauze, 10 c.m. long, rolled tightly, and completely filling the cross-section of the combustion tube, After passing the sodium hypobromite solution in the nitrogen flask, the products were led into a bottle of 7 litres capacity containing a little bromine water. A soft cork, soaked in melted spermaceti, served to connect the side tube of the nitrogen flask with that leading into the large bottle. Thus rubber tube connections were wholly avoided. The sodium hypobromite solution, together with the washings of the large bottle and combustion tube, were acidulated, evaporated, and the sulphur determined by weighing as barium sulphate.

Experiments were tried also in heating the methyl sulphide compound in carefully purified hydrogen. The same apparatus and reagents were used as in case of the employment of oxygen, the hydrogen sulphide produced being then oxidised by the sodium hypobromite to sulphuric acid. There seems, however, to be some danger of dissociation of the hydrogen sulphide and possible deposition of sulphur in the colder parts of the combustion tube. Determinations by the methods described yielded the following results:—

	Per cent.
Palladium	35·09
	35·19
Chlorine	23·75
	23·57
	23·65
Sulphur	21·57
	21·40
	21·41

The analytical results indicate for the compound the composition $PdCl_2(CH_3)_2S$, the calculated percentages in the case of such a compound being:—

	Per cent.
Palladium	35·41
Chlorine	23·46
Sulphur	21·22

The above formula is similar to that given by Enebuske (*Journ. Prakt. Chem.*, 1888, [2], xxxviii., 358), to the compound of methyl sulphide with platinous chloride, $PtCl_2(CH_3)_2S$. The palladium chloride methyl sulphide is quite stable in solid form. In solution it is susceptible to the same changes as those undergone by palladium dichloride. In solution it is reduced by carbon monoxide, and more slowly also by hydrogen. In the solid state it is reduced by hydrogen in the cold, with setting free of methyl sulphide and hydrogen chloride.

One hundred grms. of water dissolved at 26·1° C., 0·15 grm. of the compound. The solution in water, and also the dry substance, possess a slight odour of methyl sulphide. It is soluble in a great number of organic liquids, including benzene, ether, alcohol, chloroform, acetone, ethylene dibromide, carbon disulphide, methyl iodide, commercial amylene, and gasoline. It fuses at 124° C., solidifying again on cooling to a red crystalline mass. It seemed to be of interest to learn something

* *Journal of the American Chemical Society*, vol. xxiii., No. 4.

of the products of its decomposition by heat. For this purpose it was heated in nitrogen. At 210° an evolution of methyl sulphide began, and continued until the temperature rose to 260°, when a black residue was left, which proved on analysis to consist of nearly pure palladious sulphide. The gas escaping at the higher temperature, after being passed through water to remove any hydrogen chloride which might be present, was led through a glass tube containing sodium carbonate heated to redness. The sodium carbonate was afterwards tested and found to have absorbed chlorine. When the escaping gas was led through a solution of potassium hydrosulphide, methyl hydrosulphide was easily detected by its reactions toward ammoniacal solutions of silver nitrate and of copper sulphate. It was found that hydrogen chloride is not evolved on heating the compound. Hence, as chlorine had been found, and also the radical methyl, the compound methyl chloride was indicated. Moderately heated, therefore, the compound yields up a portion of its methyl sulphide. At a more intense heat it yields methyl chloride, palladium sulphide remaining as a residue.

As regards the constitution of the compound, it would seem that the sulphur of the methyl sulphide might be tetravalent. The formula might possibly be written :—

$$(CH_3)_2{=}S{-}Pd{-}S{=}(CH_3)_2.$$
(Cl above the Pd—S bond; Cl above the S=(CH3)2 bond)

This is improbable, however, because the compound seems to contain chlorine linked with palladium, since hydrogen reduces the dry compound in the cold, just as it reduces dry palladium chloride, yielding hydrogen chloride in both cases.

It seemed to be of interest to study other compounds of methyl sulphide with halides of metals. The literature of the subject is scanty, little attention having been given to compounds of this class, since Loir (*Ann. Chem. u. Pharm.*, 1853, lxxxvii., 369; *Comptes Rendus*, xxxiv., 1095), in 1853, described the compounds of methyl sulphide with mercuric chloride and iodide, and with platinic chloride.

For the preparation of the compounds described in this paper, it was necessary to obtain pure methyl sulphide. This was made by the method of Klason (*Ber. d. Chem. Ges.*, 1887, 3406), by distilling a mixture of sodium methyl sulphate with sodium sulphide.

Compound of Methyl Sulphide with Mercuric Chloride.

On adding methyl sulphide to a solution of mercuric chloride, a bulky precipitate of a white colour is produced, which is seen under the microscope to be made up of indistinct crystalline needles. Exposed in a dry state to sunlight, the substance becomes somewhat darker in colour. If preserved for some time in the solution in which it has been formed, it assumes a much more decidedly crystalline character. It is slightly soluble in water, and more soluble in alcohol. The solution has a slight odour of methyl sulphide. It is slightly soluble in chloroform, carbon disulphide, ethylene dibromide, commercial amylene, benzene, acetone, and in petroleum gasoline. The solution in water yields a heavy yellow precipitate with caustic alkalis, and in other respects the reactions in solution are similar to those of mercuric chloride.

Its melting-point varies with the rate of heating, as it undergoes partial decomposition, losing some of its methyl sulphide. When heated rather rapidly the lowest melting-point observed was 150—151°, but if the heat is applied more slowly, its colour grows darker, and as the result of a partial decomposition it melts at a varying and much higher temperature.

Heated in purified nitrogen it gives off methyl sulphide at about 150°, and at 170° white needle-shaped crystals form as a sublimate. No sulphide of mercury is formed as a result of heating. In the analysis of the compound the sulphur was determined by combustion in oxygen, as described in case of the palladium compound. Mercury was determined by precipitation of the aqueous solution by hydrogen sulphide, and weighing as mercuric sulphide. Chlorine was determined by decomposition of the compound by zinc in presence of water, and titration by silver nitrate solution. The results of the analysis are as follows :—

	Per cent.
Mercury	64·27
	64·07
	64·19
Chlorine	22·26
	22·68
	22·66
Sulphur	6·63
	6·84
	6·76
	6·73

Other determinations were made in the case of the same compound after crystallising from alcohol. The results were :—

	Per cent.
Mercury	64·41
	64·31
Chlorine	22·60
	22·53

The calculated percentages in the case of a compound having the formula $3HgCl_2{,}2(CH_3)_2S$ are as follows :—

Mercury	64·63
Chlorine	22·70
Sulphur	6·42

Loir (*loc. cit.*) assigns to the compound, obtained on adding methyl sulphide to mercuric chloride, the formula $HgCl_2(CH_3)_2S$. Analyses have been made of many preparations of the mercuric chloride methyl sulphide compound, but in no case has a product been obtained having the composition stated by Loir.

(To be continued).

THE DETERMINATION OF PHOSPHATES IN POTABLE WATERS.*

By A. G. WOODMAN and L. L. CAYVAN.

The estimation of phosphates is a part of the sanitary examination of waters which has been somewhat neglected in the past, doubtless because the ordinary methods of determination are quite tedious, and because the exact significance to be attributed to the presence and amount of phosphates is a question still in abeyance. There can be no question, however, in consideration of the probable decomposition and oxidation of the organic phosphorus compounds in animal excretions, that an excessive amount of phosphates in a water, unless otherwise accounted for, is an indication of pollution. If, then, the amount could be estimated, by a method sufficiently simple and rapid, enough data might readily be gathered to render the determination of much greater value than at present. Especially would this be true in comparing several waters from the same locality.

Repeated trials of methods which have been proposed have shown that there is none which is perfectly satisfactory for accurate and rapid work. The extremely small quantities of phosphate found even in polluted waters would seem to preclude the use of gravimetric methods. Such methods, however, have been used. Hehner (*Analyst*, iv., 23; and v., 135), and also Harvey (*Analyst*, 1880, 197), concentrate a large quantity of the water and determine the phosphate gravimetrically as ammonium phosphomolybdate. All gravimetric methods are objectionable on account of the time required. Furthermore, not being very delicate, they necessitate considerable con-

* Contributions from the Laboratories of the Massachusetts Institute of Technology. From the *Journal of the American Chemical Society*, xxii., No. 2.

centration, which, as will be shown later, almost invariably occasions a loss of phosphate. Phipson (Chemical News, lvi., 251) precipitates the phosphate from a large volume of water by means of alum and an excess of ammonia, making the final precipitation with ammonium molybdate. The process is a long one, and experiments with a more delicate method showed that the precipitation of the phosphate is not complete.

On the whole, the colorimetric methods seem best adapted for the determination. Several such methods have been proposed, based on the colour given to dilute phosphate solutions by ammonium molybdate in the presence of nitric acid. Lepierre (*Bull. Soc. Chim.*, 1896, xv., 1213) evaporates a litre of water, dehydrates the silica by repeated evaporations with nitric acid, ignites strongly, and filters. The phosphate in the filtrate is estimated colorimetrically by ammonium molybdate. Jolles and Neurath (*Monatshefte*, 1898, xix., 5) use potassium molybdate instead of the ammonium salt, and Jolles (*Archiv. f. Hygiene*, 1899, xxxiv., 22) has applied the method to the determination of phosphoric acid in water, removing the silica from the residue obtained by the evaporation of a litre of water by ignition at 130° C. These methods are open to the same objections as the gravimetric methods, namely, that by requiring the evaporation of large quantities of water, they introduce serious liability to error and are too tedious to be of general use. Furthermore, the temperature at which the residue should be ignited to remove silica is a matter of importance, especially when dealing with small amounts. In view of these considerations, it was deemed advisable to make a critical study of the colorimetric methods.

Apparatus and Reagents.

Ammonium Molybdate.—50 grms. of the pure neutral salt were dissolved in a litre of distilled water.

Nitric Acid (sp. gr. 1·07).—Approximately one part of acid (sp. gr. 1·42) to five parts of water.

Standard Phosphate Solution.—0·5324 grm. of pure crystallised sodium phosphate ($Na_2HPO_4.12H_2O$) was dissolved in freshly distilled water, 100 c.c. of nitric acid (1·07) added, and the whole diluted to 1 litre. This solution is diluted to make the standards. 1 c.c. = 0·0001 grm. P_2O_5. The solution keeps without change for several months if preserved in well-stoppered bottles of hard glass; after a longer time it becomes slightly stronger, owing to the silica dissolved from the glass.

Standard Silica Solution.—About 5 grms. of precipitated and washed silica were dissolved in an excess of sodium hydroxide made from metallic sodium. The solution was made faintly acid with nitric acid, diluted to a definite volume, and the silica determined in an aliquot part. The standard solution was made by diluting this strong solution until 1 c.c. = 0·001 grm. SiO_2.

It was found that sodium or potassium molybdate offered no particular advantages over the ammonium salt. The colour obtained was no more intense and was distinctly greener, which made the reading of the standards much more difficult. It was found also that for a given amount of the phosphate solution the depth of colour and the rapidity with which it developed depended to a certain extent upon the quantity of reagents used. The best results were obtained by the use of 4 c.c. of the ammonium molybdate solution and 2 c.c. of the nitric acid.

For comparing the colours the ordinary Nessler tubes were used at first, but it was found that if tubes of too small diameter were used the colours were not easily read; if of too large diameter the delicacy of the reaction is considerably decreased. The tubes which have been found most satisfactory have a capacity of 100 c.c. They are of hard white glass, about 2·5 c.m. in diameter and 24 c.m. long to the 100 c.c. mark. The colour is a rather difficult one to read closely, and for very accurate readings probably some form of colorimeter could be used to advantage. For any but the most refined work, however, it will be found amply sufficient to compare the tubes by a north light against a reflecting white surface, such as a pure white unglazed porcelain tile supported at an angle of about 40°. This procedure was followed in all this work, and was found most practical where a number of tubes are to be compared rapidly.

Using no greater precautions than those just described, the delicacy of the test is considerable. If care is taken to choose two tubes, identical in all respects, it is possible to detect 0·002 c.c. of the standard phosphate solution in 50 c.c. of water. If the tubes are heated to 60° C. 0·001 c.c. can be read. The delicacy of the reaction is therefore sufficient to show the presence of 1 part of phosphate as P_2O_5 in 500,000,000 parts of water. On the other hand, comparatively large quantities of phosphate may be present in 50 c.c. of water, without causing precipitation or turbidity on the addition of the reagents except after standing a considerable time. On account of the difficulty in matching the more intense colours, no higher standard than 10 c.c. of the standard solution in 50 c.c. of water is ever used, and it has been determined by direct experiment that a standard as high as this will not become turbid at room temperature for twelve or fifteen hours. The colour of the phosphate standard is an additive property; it makes no difference apparently whether the higher standards are made up directly or by the addition of more of the standard solution to the lower standards.

The question of the permanency of the phosphate standards was one of the first ones investigated. Lepierre, in the article previously cited, stated that the phosphate standards can be preserved for several months without change. Careful comparison of a number of standards from day to day, however, showed that this was not strictly true. The change in some of the higher standards, while slight, was still distinctly noticeable when carefully observed, and in others, especially the lower ones, the colour faded so much in two or three days that the standards were rendered useless. Nor was any other substance found giving the right colour which was suitable for the preparation of permanent standards. The most satisfactory was a dilute solution of picric acid, which gave a yellowish green colour very similar to the phosphate colour. But it was found impossible to keep even these standards in glass tubes, since the solvent action on the alkali of the glass was sufficient to form a slight amount of the alkali picrate, which has a more intense colour than the picric acid itself; hence, the standards slowly increased in colour. The attempt was therefore abandoned, and fresh phosphate standards were used for all comparisons.

Study of the Phosphate Reaction.

For a given volume of water and a definite amount of reagents the depth of the phosphate colour is a function of two factors, namely, the amount of phosphate present and the temperature. To determine the exact effect of the latter for the conditions employed in this work, readings of various phosphate standards were made at different temperatures. Differing amounts of the standard solution were diluted to 50 c.c., and, after the addition of the reagents, were heated gradually in a water-bath from 20° to 60° C. Readings were taken every 5°. If the reagents are added after heating, the colours are not so clear. The heating was not carried beyond 60°, because above this temperature the standards become cloudy and the higher standards tend to precipitate. The maximum colour is given between 90° and 100°, but the tendency to precipitation renders the reading at this temperature impracticable. The most satisfactory colours are obtained at 20—30°, practically at room temperature. A variation of a few degrees causes only a slight error. The results are given in the accompanying table.

The results shown graphically show slight irregularities, due to the difficulty of reading exactly. The increase in colour with increased temperature is considerable, double in the higher standards. All of the standards on cooling go back to less than their original colour. No case of

Amounts phosphate added.	25°.	30°.	35°.	40°.	45°.	50°.	55°.	60°.
6 c.c. ..	6·2	7·2	7·7	8·2	8·7	9·6	—	10·2
	6·2	7·2	7·8	8·3	8·7	10·2	10·4	10·7
	6·2	7·7	8·2	9·0	9·2	9·7	10·4	10·3
Average ..	6·2	7·3	7·6	8·5	9·0	9·8	10·4	10·5
5 c.c. ..	5·1	5·9	6·6	7·3	7·8	8·0	8·6	9·6
	5·1	5·3	6·1	7·2	7·9	8·4	8·6	9·4
	5·1	5·2	6·3	7·1	8·0	8·3	8·7	8·9
	5·1	5·6	6·6	7·0	7·8	8·5	8·6	9·2
Average ..	5·1	5·5	6·4	7·2	7·9	8·3	8·6	9·2
4 c.c. ..	4·1	4·7	5·1	5·4	6·4	6·6	6·9	7·1
	4·1	4·8	5·1	5·5	6·4	6·5	6·8	7·3
	4·1	4·8	5·1	5·5	6·4	6·6	7·0	7·4
Average ..	4·1	4·7	5·1	5·5	6·4	6·6	6·9	7·2
3 c.c. ..	3·1	3·4	3·9	4·5	5·1	5·7	5·8	6·2
	3·4	3·7	4·4	4·7	5·2	5·3	5·7	5·9
	3·2	3·7	3·9	4·3	4·9	5·4	5·5	6·2
Average ..	3·2	3·6	4·1	4·5	5·1	5·5	5·7	6·1
2 c.c. ..	2·2	2·5	2·7	2·9	3·1	3·4	3·6	3·9
	2·2	2·5	2·8	3·1	3·2	3·4	3·7	3·9
	2·4	2·6	2·9	3·0	3·3	3·4	3·5	3·9
Average ..	2·2	2·5	2·8	3·0	3·2	3·4	3·6	3·9
1 c.c. ..	1·1	1·2	1·4	1·5	1·5	1·7	1·9	1·9
	1·1	1·2	1·3	1·4	1·5	1·7	1·8	1·8
	1·1	1·2	1·4	1·5	1·5	1·5	1·7	2·0
Average ..	1·1	1·2	1·4	1·4	1·5	1·6	1·8	1·9
0·7 c.c..	0·75	0·80	0·85	0·95	1·1	1·2	1·25	1·27
	0·75	0·80	0·85	0·90	1·05	1·15	1·25	1·28
	0·75	0·80	0·83	0·95	1·05	1·15	1·20	1·25
Average ..	0·75	0·80	0·85	0·93	1·05	1·17	1·22	1·26
0·5 c.c..	0·60	0·65	0·70	0·80	0·90	0·95	1·05	1·10
	0·60	0·60	0·65	0·75	0·85	0·90	0·95	0·95
	0·60	0·65	0·70	0·75	0·85	0·85	0·95	0·95
Average ..	0·60	0·65	0·70	0·77	0·87	0·90	0·98	1·01
0·4 c.c..	0·45	0·50	0·55	0·65	0·70	0·75	0·80	0·80
	0·45	0·55	0·55	0·57	0·60	0·65	0·70	0·70
	0·45	0·55	0·55	0·58	0·65	0·67	0·70	0·70
Average ..	0·45	0·53	0·55	0·60	0·65	0·68	0·72	0·72
0·3 c.c..	0·33	0·36	0·39	0·44	0·48	0·58	0·63	0·68
	0·33	0·36	0·39	0·45	0·50	0·55	0·60	0·65
	0·33	0·36	0·39	0·44	0·54	0·58	0·60	0·65
Average ..	0·33	0·36	0·39	0·44	0·51	0·57	0·61	0·66
0·2 c.c..	0·23	0·27	0·31	0·32	0·34	0·37	0·38	0·39
	0·23	0·27	0·30	0·33	0·33	0·36	0·38	0·39
	0·23	0·27	0·30	0·33	0·34	0·37	0·38	0·39
Average ..	0·23	0·27	0·30	0·33	0·34	0·37	0·38	0·39
0·1 c.c..	0·11	0·13	0·14	0·16	0·17	0·18	0·19	0·20
	0·12	0·13	0·14	0·16	0·17	0·18	0·19	0·20
Average ..	0·11	0·13	0·14	0·16	0·17	0·18	0·19	0·20

precipitation occurred, although some of the highest standards were too turbid to be read easily.

Several of the methods previously proposed for the determination of phosphates involve the concentration of the water, followed by heating at various temperatures. Preliminary experiments had shown the liability to loss during such procedure, and the point was further investigated. One litre of water, containing 5 c.c. of phosphate solution and 2 c.c. of nitric acid, was evaporated to dryness; a loss of 16 per cent of the phosphate occurred. Phosphate standards made up in a volume of 50 c.c., with varying amounts of nitric acid, were evaporated to dryness, and some of them heated in an air-bath at 100° for periods varying from fifteen minutes to two hours. A loss of phosphate always occurred whether done in platinum or porcelain dishes. Other standards were evaporated and heated at 135° C., still others were ignited over a free flame; a loss was found in all cases. An idea of the magnitude of the loss may be gained from the following figures:—

Evaporated without Nitric Acid and Heated One Hour at 100°.

In porcelain dishes—						
Amount added ..	0·1	0·2	0·5	1·0	2·0	5·0
Amount found ..	0·1	0·18	0·45	0·75	1·8	4·9
In platinum dishes—						
Amount added ..	0·1	0·2	0·5	1·0	2·0	5·0
Amount found ..	0·07	0·12	0·4	0·85	1·8	4·9

Evaporated as above, but Heated One Hour at 135°.

In porcelain dishes—						
Amount added ..	0·1	0·2	0·5	1·0	2·0	5·0
Amount found ..	0·0	0·0	0·0	1·0	1·5	4·0
In platinum dishes—						
Amount added ..	0·1	0·2	0·5	1·0	2·0	5·0
Amount found ..	0·0	0·0	0·1	0·6	1·3	2·7

In all cases where nitric acid was used and the residue was heated at 100°, the loss on a 2 c.c. standard was from 0·02 to 0·22 c.c. greater the more acid used. Where the ignition was made over a free flame the loss varied from 25 to 50 per cent, highest in the low standards. Without the addition of nitric acid the loss on evaporation was very irregular. In the presence of a definite quantity of acid the loss was more nearly constant. Without going into great detail, it may be said that it was apparent that the loss was due to some change taking place while the solution is dilute and hot. The total loss occurs usually during the concentration of the solution to one-half its volume.

(To be continued).

CORRESPONDENCE.

THE SOUTH AFRICAN COLLEGE.

To the Editor of the Chemical News.

SIR,—With reference to a paragraph in your issue of April 26 (CHEM. NEWS, lxxxiii., 194), wherein you incidentally observed that Mr. R. T. Smith, B.A. (Cantab.), recently appointed Principal of the Northern Polytechnic Institution, "organised and equipped the South African College at Cape Town, and acted as Professor of Mathematics and Physics in the College for some years," I am asked by the Council of the College to inform you that the South African College was founded over seventy years ago—in 1829.

A few years ago a Laboratory for Experimental Physics was erected in connection with the Institution, and on the Building Committee, of which I had the honour of being Secretary, Mr. Smith, then recently appointed Professor of Physics, naturally occupied a most important advisory position. It is not correct to say that Mr. Smith was "Professor of Mathematics and Physics in the College." During the whole of Mr. Smith's tenure of office as Professor of Physics the mathematical chair was occupied

by the late Professor Francis Guthrie, B.A., LL.B., brother of the distinguished chemist the late Frederick Guthrie.—I am, &c.,

CHAS. F. JURITZ, M.A. (Senior Govt. Analyst),
Hon. Sec. S.A. College Union.

Government Analytical Laboratory,
Cape Town, Cape of Good Hope,
July 10, 1901.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 3, July 15, 1901.

Thermometric Examination of Solid Potassium Hydrates.—M. de Forcrand.—The author's researches show that, besides the two compounds KOH and $KOH+2H_2O$, there exist two intermediate hydrates, $KOH+0{\cdot}5H_2O$ and $KOH+H_2O$. The possible hydrates, $KOH+0{\cdot}25H_2O$ and $KOH+1{\cdot}5H_2O$, also are on the straight lines joining neighbouring points. The heat of fixation of 0·5 H_2O liq. on to solid KOH is +6·30 cal., or +12·60 calories per molecule. The fixation of a second half molecule of water whilst passing to the compound $KOH.H_2O$ only evolves +3·15 calories, or +6·30 calories per molecule. Finally, the heat evolved for the fixation of the entire molecule on to $KOH.H_2O$ to give $KOH.2H_2O$ is only +3·04 cal. The three numbers +12·60, +6·30, and +3·04 are exactly in the proportion 4 : 2 : 1. These facts explain why potash, when used to absorb water (from gases, for instance), should be in the form KOH; specimens of commercial "pure potash" usually have about the composition $KOH+H_2O$, and are therefore very imperfect dehydrating agents. Apparently the first portions of water fixed (up to 0·25 H_2O) evolve less heat than the following portions (from 0·25 to 0·50 H_2O).

Iodine-phenyl Ethereal Derivatives.—P. Brenans.—In a previous paper the author relates the conditions under which iodine gives with phenol the di-iodophenol, $OH—C_6H_3—I_2.1.2.4$, and the tri-iodophenol, $OH—C_6H_2—I_3.1.2.4.6$. He now describes the methods of preparation and the properties of a number of ether oxides and ether salts obtained from these two iodine compounds—(1) Ether oxides of di-iodophenol, *e.g.*, propylphenylic, isopropylphenylic, and allylphenylic ethers; (2) ether oxides of tri-iodophenol, *e.g.*, tri-iodoanisol, tri-iodophenethol, propylphenylic, allylphenylic, and benzylphenylic ethers; (3) ether salts of di-iodophenol, *e.g.*, neutral succinic and neutral phthalic ethers; (4) ether salts of tri-iodophenol, *e.g.*, acetic ether and benzoic ether.

Action of Pyridic Bases on the Tetrahalogen Benzoquinones.—Henri Imbert.—When some acetic ether is placed in a flask with a reflux condenser, and, on bringing this to boiling-point, chloranile is added with some pyridine, the liquid first becomes red, then a reaction begins; acetic acid is added, and a red body is obtained from this mixture which apparently has the formula $HO—C_5H_2N=C_6Cl_2O_2$.

New Decompositions of Methyl-*c*-butyrylacetylacetate.—A. Bongert.—In a recent paper the author explained the action of hydrazine on *o*- and *c*-methyl butyrylacetyl acetate. Having had occasion to re-examine the reaction on the latter body, he was surprised to find that he obtained totally different results. The varying reactions were due to the fact that in the first experiments he employed hydrazine in the form of acetate, obtained by double decomposition between its sulphate and sodium acetate in very dilute solution. In the second experiment, the action took place between an aqueous solution of hydrazine hydrate and butyrylacetylacetate dissolved in ether.

Pyromucic and Isopyromucic Acids.—M. Chavanne.—Besides pyromucic acid, Limpricht found in the dry distillation products of mucic acid a new acid, isopyromucic acid, which he distinguished by the green colour which it gives with ferric chloride. The author undertakes an examination of the properties of these bodies. The first experiments resulting in a method of sharply distinguishing between the two acids, and a method of separating the isopyro- from pyromucic acid.

Dichlor-orthoxylenes.—L. Ferrand.—By the action of chlorine on orthoxylene in presence of iodine, Claus and Kantz obtained a little of the mono- and trichlor-orthoxylenes and some 4—5-dichloro-orthoxylene in the form of a liquid boiling at 227°. This liquid, when oxidised by dilute nitric acid, gives an acid which seems to be 4—5-dichlorophthalic acid, because, if distilled with soda-lime, it gives ortho-dichlorobenzene, which melts at 183°. They also obtained, as well as this liquid compound, a certain quantity of a solid isomer fusing at 73°, which they did not examine. The author continues these researches, and determines the composition of this isomer, but finds, when employing the same method as that used by Claus and Kantz, he obtains two isomers—one a liquid, dichlor-metaxylene, boiling at 221°; and the other a solid (melting-point 68°). His researches apparently show that, during the action of chlorine on orthoxylene in the presence of iodine, the three possible chlorine derivatives are obtained, and not only one as Claus affirmed.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Sympathetic Ink.—I remember reading somewhere of a certain compound which could be used as ink. Its peculiar property was that it faded out as soon as it got dry, and could only be read when damped. I have seen this done by friends and have used the fluid myself. I do not think it had anything to do with litmus or the commoner colouring matters. It must have been easy to prepare since we students could make it. If anyone can tell me how it could be done I shall be very much obliged.—W. H. S.

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THE CHEMICAL NEWS.

VOL. LXXXIV., No. 2177.

PRELIMINARY NOTE ON A POSSIBLE METHOD OF ATTAINING THE ABSOLUTE ZERO OF TEMPERATURE.

By GEOFFREY MARTIN.

THE conception of an absolute zero of temperature belongs to the nineteenth century. Previously such an idea existed only as a vague speculation.

The magnificent researches of Andrews, Cailletet, Pictet, and others on the permanent gases brought home to all this possibility in a forcible manner. Men heard with amazement that air had been reduced to a mobile liquid so intensely cold as to burn like molten lead; and for the first time they caught a glimpse of a strange cold world with its mystery and possibilities—a world hitherto scarce dreamt of.

Matter without heat! The idea seemed almost absurd to the general public. Yet towards the end of the last century scientists were rapidly reducing it to that condition. Oxygen, air, nitrogen, all were liquefied successively, and a temperature less than 100° C. from the absolute zero was obtained. Hydrogen barred the way for a long time, and it was not until 1898 that Dewar obtained it in quantity as a beautiful, clear, colourless liquid, possessing a density only one-fourteenth that of water at 0° C. By rapidly evaporating it he obtained a temperature only 13—14° C. from the absolute zero itself—a notable achievement.

By the use of liquid helium a still lower temperature will be probably obtained, but the absolute zero itself is not attainable by such methods, for even the most volatile gas will become solid and lose all vapour tension long before this point is reached. Some other method of making matter yield up its energy must therefore be devised.

Perhaps the phenomena of thermo-electricity will be of use. Peltier showed that if a current be passed across an antimony-bismuth junction in one direction heat is developed, and in the reverse heat is absorbed, and an appreciable cooling effect obtained. Similarly in the case of any two other metals heat is generated if the current traverses the surface of contact in one direction, and is consumed if it passes in the opposite direction—the quantity of reversible heat being in each case proportional to the strength of the current, and to a coefficient π depending on the nature of the metals and their temperature.

So that, in general, if r is the resistance of the part of the circuit containing the junction, the energy converted into frictional heat is c^2r, and the energy converted into reversible heat is $c\pi$. Hence, if H be the quantity of heat produced in t secs., we have J. H. $= c\pi t + c^2rt$. By making a small hole at the junction of a bismuth and antimony bar, in which was placed a drop of water and a small thermometer, the whole being cooled to zero, Lenz found that when a current was passed from bismuth to antimony the water was frozen, and the thermometer sank to $-3{\cdot}5°$ C.

Opposing this fall in the junction's temperature there are in general two influences.

Firstly, when a current is passed through a conductor a frictional generation of heat occurs, which tends to mask the cooling effect. Secondly, when one part of a circuit is at a much lower temperature than the other parts, heat will flow by conduction from the hotter to the colder parts, and thus again oppose further cooling.

When a stationary low temperature has been reached by the junction, we must imagine that as much heat is absorbed by the current in unit time as is imparted to the junction by means of both of those influences I have mentioned working together.

If, therefore, we could diminish or do away with these, a very great cooling effect could be obtained.

The frictional heating could be eliminated to a great extent by cooling the whole to the lowest temperature attainable by the use of liquid hydrogen. Recent experiments by Profs. Fleming and Dewar show that an astonishing fall in the specific resistance of most metals takes place at very low temperatures. Thus, the specific resistance of copper and iron fall from 1564 and 9115 respectively at 0° C., to 289 and 1200 at $-205°$ C.; while at a temperature only 20° lower these numbers become 144 and 660—*i.e.*, the specific resistance at $-220°$ C. is actually half that at $-200°$ C. (*vide* Foster and Atkinson's "Electricity and Magnetism," 1896, p. 162). Such an enormous diminution in the specific resistance leads one to expect that at only 13—14° C. from the absolute zero—the lowest temperature yet attained by Dewar—the resistance would be practically negligible, so that the term c^2rt in the above expression would become extremely small, even when *currents* are employed considerably more powerful than those which can be used at ordinary temperatures for producing the Peltier effect. If the quantity π remained appreciably large it is quite possible that matter could by such means be chilled almost to the absolute zero without the masking effect of frictional heat becoming sensible.

The second influence, namely, the flow of heat by conduction from the hotter parts of the bar to the cold junction, could be eliminated by avoiding a sensible temperature difference between the chilled junction and the rest of the circuit. For instance, each small section of the main circuit could be cooled simultaneously with the junction by means of a number of other chilled thermo-electric junctions. By the use of some such contrivance the temperature of the junction need never become very much lower than that of the rest of the circuit. The coefficient π would certainly alter with the temperature. Unless it completely vanished for all bodies at very low temperatures such an effect could be corrected by properly choosing the metals forming the junctions.

At the absolute zero molecular motion has completely died away; matter even in this condition is not the cold dead mass it is sometimes pictured to be, but is still quivering with motion. Each individual atom is itself a seething universe of still smaller particles, as has been demonstrated by J. J. Thomson's work on Ions. The emanations from radio-active matter have also proved to be particles enormously smaller than atoms, shot forth from the molecule with a velocity of many tens of thousands of miles a second.

At the absolute zero all that has occurred is a disappearance of relative motion among the particles of matter of a molecular scale of magnitude.

For vastly smaller and vastly greater particles, relative motion or "temperature" still exists. It is this latter property that will make the attainment of the absolute zero such a vitally important achievement. For it is only in matter in this condition that we can study internal atomic vibrations free from secondary disturbances caused by the approach and recedence of neighbouring atoms.

The measurement of the molecular refraction, dispersion, rotation of the plane of polarisation, and other similar constants for different chemical compounds when reduced to this condition, will certainly lead to most important discoveries regarding the structure of atoms and molecules.

For it is only when all bodies are in such a state that the full atomic effect of each atom in a molecule, unmasked by artificial clashing and jarring, can be obtained.

Bristol, August 3, 1901.

THE ASSAYING OF COMPLEX GOLD ORES.*

By ERNEST A. SMITH, Assoc.R.S.M., F.C.S.,
late Assistant Instructor in Assaying, Royal School of Mines, London.

(Continued from p. 64).

Pyritic Ores (continued).

Method (*b*).—The oxidation of the pyritic material in an ore by the use of nitre during fusion is preferred by some assayers, as it is somewhat more expeditious than oxidation by roasting. The method, however, is limited in its application to gold ores, as the use of large quantities of nitre is to be deprecated, since the contents of the crucible are very liable to boil over owing to the energetic effervescence which takes place.

Ores consisting chiefly of pyritic material frequently require more than twice their own weight of nitre to effect complete oxidation; and as it is generally necessary, in the case of gold ores, to use from 30 to 50 grms. of ore for assay, the use of nitre becomes impracticable.

If nitre is employed for effecting the oxidation of pyritic material the approximate quantity needed is ascertained by the methods subsequently given for the assay of antimonial ores by this process, and the remarks on the use of nitre there given are equally applicable to pyritic ores.

The approximate quantity of nitre necessary to oxidise various "sulphurets" has been arrived at by experiment, and is given in the following table:—

Approximate Oxidising Effect of Nitre.

	Parts of nitre required to one part of "of sulphuret."
Iron pyrites	about 2 to 2½ parts
Mispickel, Copper pyrites, Fahlerz, Zinc blende	„ 1½ to 2 „
Antimonite	„ 1½ „
Galena	„ ⅔ „

When the nitre has completed its action the product consists mainly of metallic oxides, and the ore is fluxed accordingly on the lines indicated for basic ores.

Method (*c*).—Fusion of gold ore with lead oxide alone is adopted by some assayers in cases where the sample to be operated upon contains only an amount of pyritic material sufficient to yield a convenient quantity of lead for cupellation. When this method is used the lead oxide must be in excess, as it not only serves as an oxidising agent, but also acts as a flux for the gangue of the ore and the oxides resulting from the oxidation of the pyritic material. Silica requires nearly 5 parts of litharge, and the metallic oxides require from 2 to 10 parts to form fusible compounds. In this case, which applies to ores containing about 10 per cent or less of pyritic material, a charge of from 30 to 50 grms. of ore is usually employed, and is fused with from four to five times its weight of red-lead or litharge. Charcoal powder is added in cases where the proportion of sulphides is not sufficient to give the required weight of lead. Red-lead is used in preference to litharge on account of the larger amount of oxygen it contains.

As the quantity of lead oxide requisite for the decomposition of a sulphide is considerable, very pyritic ores cannot be conveniently assayed by this method unless sufficiently rich to allow of comparatively small quantities of material being operated upon. The proportion of lead oxide required to effect complete desulphurisation varies according to the nature of the sulphide, but in all cases is large. When less than the requisite quantity of lead oxide is used, only a portion of the sulphide is decomposed, and a corresponding quantity only of lead reduced, whilst the remainder of the sulphide forms, in combination with the litharge and metallic oxide which is produced, a compound belonging to the class of oxysulphides which are generally very fusible (Mitchell). If oxysulphides are present to a large extent in the slag they cause the retention of appreciable quantities of the precious metals.

All sulphides, arseno-sulphides, &c., are readily oxidised by lead oxide with the production of a quantity of lead equivalent to the oxidisable substances present; this method of assay is therefore inconvenient on account of the large quantity of lead it produces, which needs to be reduced by scorification before it can be cupelled. The method may be modified in some cases by adding a little nitre to the mixture to assist in oxidising the sulphur, &c. One grm. of nitre is equivalent in oxidising effect to 20 grms. of red-lead or 26 grms. of litharge.

Method (*d*).—In this method metallic iron is used as a desulphurising agent, the iron combining with the sulphur to form ferrous sulphide, which passes into the slag. ($FeS_2 + Fe = 2FeS$).

The method can only be satisfactorily applied to ores containing not more than about 25 to 30 per cent of pyrites. When the percentage of pyrites is much above this the results obtained are far from trustworthy, and the method cannot be recommended. A moderate quantity of sulphur may be successfully converted into iron sulphide and dissolved in the slag, but with ores containing excess of pyrites it is difficult to effect complete reduction by this method, even when large quantities of metallic iron are added to the charge; the lead button obtained is always more or less brittle, owing to the presence of sulphur, and is frequently accompanied by a layer of regulus. In cases where a regulus is produced it is best to repeat the assay by the method of oxidation by roasting previous to fusion.

The following quantities are convenient for ores containing 30 per cent of pyrites or less:—

Ore	50 grms.
Red-lead	40 to 50 „
Charcoal powder	2 to nil „
Borax	10 to 15 „
Sodium carbonate	40 to 50 „

With the addition of metallic iron.

The slags should be strongly alkaline, and to secure this end an excess of sodium carbonate should be employed in the charge.

To ensure the complete collection of the precious metals a comparatively large button of lead should be obtained from the fusion. From the charge given, a lead button would be obtained weighing from 30 to 40 grms.

The fusion should be performed at a comparatively low temperature, and the crucible should remain in the furnace for about five minutes after the contents are in tranquil fusion. The iron is then taken out and examined while hot, and should any shots of lead be found adhering to it, they must be washed off by immersing it in the molten slag, after which it is withdrawn, and the crucible is left in the furnace for a few minutes longer. The crucible is then removed from the furnace, and its contents poured into a mould in the ordinary way. When arsenic is present the iron will decompose the arsenical compound with the formation of a speiss, which separates as a hard greyish-white layer on the surface of the button of lead. The separation of a small quantity of speiss may be disregarded, as it seldom retains an appreciable quantity of gold, but if large quantities of arsenic are present, it must be eliminated by previously roasting the ore with the precautions mentioned in the treatment of arsenical ores described subsequently.

Hard and somewhat brittle lead buttons will be obtained from ores containing copper sulphides, as these compounds are partially reduced to the metallic state by iron and lead, the copper passing into the lead button, and causing trouble in the cupellation unless previously removed by scorification. In this case a cupriferous regulus, which retains appreciable amounts of gold and silver, is also frequently formed. Ores containing much copper or antimony must be treated by special methods described

* Abstract of Paper read before Institution of Mining and Metallurgy, May 15, 1901.

subsequently. The presence of antimony compounds will produce brittle lead buttons, and give rise to the formation of a scoria on the cupel, which tends to retain part of the precious metals and leads to unsatisfactory results.

Arsenical Ores.—Arsenic is most frequently associated with gold ores as mispickel (arsenical pyrites), and occasionally as oxides.

Its presence gives rise to the production of compounds which tend to diminish the accuracy of the assay. It is therefore necessary to eliminate the arsenic, and this is usually effected by roasting or by the use of nitre. Much diversity of opinion exists as to which is the better of these two methods, many assayers hesitating to roast arsenical ores on the ground that, owing to the volatile character of arsenic, mechanical loss of the precious metals is caused. It has been pointed out that this may occur when too high a temperature is employed at the outset, thus causing a rapid disengagement of the volatile constituents of the ore, but with due precaution this may be avoided. The formation of arseniates is mostly to be feared, as they are liable to remain undecomposed, and cause loss of gold and silver in the slag during fusion. The ore is roasted, with all the precautions previously mentioned under pyritic ores, until completely oxidised; then from 5 to 10 per cent of charcoal powder is added, and the roasting continued until all the carbon is burnt out. Owing to the rapidity with which arsenic vapourises, great care is needed in regulating the temperature.

An attempt to eliminate arsenic by rapid oxidation would be attended with the danger of converting it into arseniates of the metals present in the ore, such as iron, copper, lead, &c. When once formed, arseniates are not readily decomposed, as they resist a high temperature, and are only slowly converted into sulphates at a red heat by the sulphuric acid formed during the later stages of the roasting.

The product obtained by roasting the ore is composed largely of ferric oxide, and is fluxed according to the directions given for the treatment of basic ores. When the oxidation of the arsenical compounds is effected by means of nitre, the ore may be treated by the nitre methods described under "Antimonial Ores."

(To be continued).

CRITICAL REMARKS ON M'KENNA'S METHOD OF ANALYSIS OF TUNGSTEN AND CHROME STEELS. THE DETERMINATION OF TUNGSTIC ACID AND SEPARATION FROM SILICA.*

By OTTO HERTING, Philadelphia.

In the *Proceedings of Engineers' Society of Western Pennsylvania*, 1900, xlvii., p. 1186, the "M'Kenna Method of Analysis of Chrome and Tungsten Steels" was described in the form of an abstract from the Chemical News, lxxxii., 67. That this method leads to incorrect results in the cases of silicon, sulphur, and tungsten, I will attempt to prove, and, at the same time, give the methods by which correct results may be obtained.

As regards the determination of silicon, Mr. M'Kenna seems to be unaware that, by the solution of an iron containing silicon in hydrochloric acid, there is always volatile SiH_4 formed; hence the silicon determination comes out too low. Every iron and steel chemist always uses nitric acid, or nitric acid and sulphuric acid, to dissolve when silicon is to be determined.

The determination of sulphur, which M'Kenna unites with that of silicon, must also lead to incorrect and low results, which I have already proven in the article, "The Useful Methods for the Determination of Sulphur in Iron Pyrites," &c. (*Chem. Ztg.*, 1899, 23—25). In this article, based on the classical works of Campredon and Schulte (*Stahl in Eisen*, 1897, No. 12), I have maintained:—"All methods which rest on the evolution of H_2S give too low results, unless a combustion tube heated to a low red heat is interposed." These articles have not been reproduced in the Chemical News, and for this reason, therefore, have probably not come to the knowledge of Mr. M'Kenna.

For the analysis of tungsten iron alloys, the exact determination of tungsten and the separation from silica is of the greatest importance. As regards the separation from SiO_2 of WoO_3 I can maintain, on the ground of many experiments which I have made with quantitative mixtures of pure tungstic acid and pure ignited silica, that the methods given in the text-books, which rest on the volatilisation of SiO_2 by HFl, are incorrect. There must be formed by the ignition of tungstic acid and silica a silico-tungstic acid, which, treated with HFl, is volatile.

For the analysis of a ferro-tungsten I use the following method:—1·0 to 3·0 grms. of the sample is treated with aqua regia, evaporated to dryness twice on the water-bath with HNO_3, dried at 120°, taken up with dilute HNO_3, filtered, and washed with the same dilute acid; there remains insoluble WoO_3,SiO_2, together with a little iron. In order to remove the latter the residue is fused with Na_2CO_3, taken up with water, the iron filtered off (this is afterwards examined for silica); the filtrate is evaporated to dryness twice with HNO_3, taken up with dilute HNO_3 and filtered. The residue, consisting of SiO_2 and WoO_3, is ignited and weighed, then carefully fused with five times its weight of $KHSO_4$, and the fusion digested with a weak ammonium carbonate solution, whereby the WoO_3 goes into solution, and a smooth separation is obtained.

Certainly, this method requires much time, but it gives satisfactory results. . . . .

In conclusion, I would like to mention that, while Mr. M'Kenna dissolves so readily tungsten chrome iron alloys in acids, I have never been able to do this with chrome alloys. I have always had to make a fusion with sodium, potassium carbonate, and magnesia.

As regards the chrome determination which M'Kenna mentions, the same is already fully described in Ledebur's "Leitfaden fur Eisenhuttenlaboratorien," 1895, p. 36.

It would please me much if these lines should cause more study of the "Action of Hydrofluoric Acid on Tungstic Acid in the Presence of Silica."

* From *Proceedings of Engineers' Society of Western Pennsylvania*, xvii., No. 4. Translated from *Zeit. f. Angew. Chemie*, 1901, p. 165.

A REPLY TO THE ABOVE.

By A. G. M'KENNA.

In the seventh number of the *Zeitschrift fur Angew. Chemie* appears the above somewhat caustic criticism by Mr. Herting, of Philadelphia, on the method I use in analysing chrome and tungsten steels, described by me in a paper read before the Chemical Section of the Engineers' Society of Western Pennsylvania, in April, 1900.

Mr. Herting, who appears to prefer to obtain his chemical information from German sources, bases his criticisms on a translated abbreviated abstract of a reprint in the Chemical News, and has apparently not considered it worth while to consult the original article before criticising it. His first statement is that, by the solution of an iron in HCl, volatile SiH_4 forms, causing low results; also that "every iron and steel chemist always uses nitric acid, or nitric and sulphuric, in dissolving irons for silicon determinations." If our collection of methods used in the iron and steel works near Pittsburg had been translated into German, Mr. Herting would probably have known that in the laboratory of the largest iron and steel works in the world—that of Edgar Thomson—99 per cent of all silicon determinations are made by solution in HCl, and that at least one-half the iron and steel chemists who described their methods at our request do not use nitric acid. I would suggest that, before making any more sweeping assertions as to what "every

iron and steel chemist always does," he should obtain some slight knowledge on the subject, either by visiting the laboratories in the western end of his State, where most of the iron and steel is made, or by consulting the above collection of methods in use here. He might also refer to Fresenius, who recommends solution in HCl.

Any chemist who wishes to know whether there is the slightest truth in the statement that silicon is lost by volatilisation with HCl has only to make duplicate determinations by HCl and by HNO_3. At my request Mr. J. M. Camp, chemist at the Duquesne Steel Works, and Mr. J. A. Mohr, chemist at the Carrie Furnaces, have done this, and both have written me there is no difference in the results.

In regard to the evolution sulphur method, Mr. Herting seems recently to have discovered what has been a matter of common knowledge among the iron and steel chemists of this section for at least ten years—that is, that low results are obtained by the evolution method if the theoretical factor is used. His charitable assumption that I am ignorant of this fact, because his article of 1899 on the subject was not reprinted in the Chemical News, would not have been necessary had he taken the pains to refer to my original article, since I there plainly state that when cold acid is used lower results are obtained. (In the abstract this was not mentioned).

Mr. F. H. Williams, in November, 1892, read before this Section a paper in which he gave results showing that by the use of hot acid higher results are obtained by evolution than when cold acid is used, although these results are still a trifle below aqua regia method results. Mr. S. A. Ford, in whose laboratory I was then employed, stated during the discussion of the paper that he had known for years that part of the sulphur was evolved in a form which was not absorbed.

Dr. F. C. Phillips, who took part in the discussion, was incited thereby to investigate the question thoroughly, and published his results in November, 1895, in the *American Chemical Journal*. The classical work of Campredon and Shulte, in 1897, merely confirmed Dr. Phillips's results. In view of these facts it may well be doubted whether our knowledge on the subject would have been materially increased, even if the Chemical News had reprinted Mr. Herting's belated article based on Campredon and Shulte's classical work.

In spite, however, of the above mentioned facts, it is still customary, in the vast majority of iron and steel laboratories, to make nearly all sulphur determinations by evolution, minimising the error, as far as possible, by standardising the iodine solution against a similar iron or steel of known sulphur contents. Thus, at the Edgar Thomson Steel Works laboratory, different factors are used for the same iodine solution, according to whether the sample is a chilled iron or a pig-iron or steel.

Mr. Herting's next objection is to the separation of silica from tungstic acid by volatilisation with HFl. As far as I have been able to determine, his assumption of the formation of a volatile silico-tungstic acid is purely imaginary. Arnold, in his "Steel Works Analysis," p. 136, says:—"The alleged liability of WoO_3 to volatilise with silicon unless H_2SO_4 is present has no foundation in fact." I have treated weighed quantities of ignited silica and tungstic acid with HFl, and in no case have found a loss of tungstic acid. At my request Dr. K. F. Stahl, of the General Chemical Company, J. M. Camp, and J. A. Mohr, have investigated the matter, and all have written me there is no evidence of loss of tungstic acid on their repeating the tests.

Mr. Herting next describes his method of determining tungsten in a ferro-tungsten, which appears to be his idea of fulfilling the promise he makes in the beginning of his paper to describe the methods by which correct results can be obtained in the complete analysis of alloy steels. Of this method I will only say, life is short. It involves five evaporations, two fusions, five filtrations, one extraction, and determines tungsten.

He next complains that he has never been able to dissolve chrome alloys in acids. Can it be he has been attempting to analyse a ferro-chrome by the methods I described for chrome steels? I have dissolved many thousand samples of chrome steels in acid, and have yet to find one in which residue was not completely volatile with HFl. Perhaps Mr. Herting will explain this by assuming a volatile compound of silico-chrome with HFl?

Mr. Herting's parting remark is that the method for chromium was fully described by Ledebur, in 1895, in his "Leitfaden fur Eisenhuttenlaboratorien," p. 36. Here, again, Mr. Herting would have been spared the necessity of making this unjust accusation if he had carefully read my article in full, as he would have found I titrated chromium in a nitric acid solution after oxidation to chromic acid by potassium chlorate, an entirely different method from that described by Ledebur.

CONTRIBUTIONS TO THE SCIENCE OF THE NITROCELLULOSES.*

By G. LUNGE and J. BEBIE.

(Continued from p. 67).

We now make mention of another series of experiments, in which the ratio of nitric acid to water was kept constant, whilst the amount of sulphuric acid varied. Thus the results are only to be referred to the action of the sulphuric acid, which may be traced to two causes;—First, to the absolute influence of the sulphuric acid, and afterwards also to the diminution of the percentage of water, owing to its abstraction by the sulphuric acid. These two actions unite in producing their effect, but the greater part must be ascribed to the indirect, according to the results of the last section.

The nitric acid used had the specific gravity 1·40; the ratio $HNO_3 : H_2O$ was found to be after analysis = 184 : 100. Equal weights of this acid were now treated with varying quantities of concentrated sulphuric acid, but care had to be taken to supply water to the nitration mixture with this sulphuric acid, which was 94·91 per cent. This was compensated for by a calculated addition of nitric acid of specific gravity 1·50, so that the ratio $HNO_3 : H_2O$ was constant throughout, and the results of this nitration mixture give us a representation of the action of the sulphuric acid.

The experiments were conducted at the temperature of the room, and the time of nitration lasted twenty-four hours. In this way, nitration up to a proportion of about 33 per cent sulphuric acid was not complete; unchanged cellulose always remained. At first this seemed to us to be no drawback to the experiment. By determination of the nitrogen of the mixture, and from the determination of the unchanged cellulose with sodium methylate, the nitrogen percentage of the nitro-product should be obtained indirectly; in this way we hoped to obtain the lowest stage of nitration, and eventually to find in connection with it the smallest value for the molecular weight of cellulose.

But the cellulose determinations proved to be inexact; determinations from the same product varied between 5 to 10 per cent. These differences are due to the presence of oxycellulose; for, by the influence of the dilute acids, the cellulose is completely or partially converted into oxycellulose. Part of the unchanged cellulose must be dissolved by the slightly alkaline sodium methylate solution, and, in consequence, the determinations of the cellulose appear too low.

In order to obtain a more exact conclusion as to the oxidising action in the nitration mixture, an attempt was

* *Zeitschrift fur Angewandte Chemie*, 1901, Heft 20.

made to trace quantitatively the formation of oxycellulose in different nitration mixtures, by a determination of the affinity for basic colour stuffs. Formerly 0·5 grm. of the substance was warmed on the water-bath for an hour with 150 c.c. of a 5 per cent methyl-blue solution in a beaker covered with a watch-glass, after cooling 100 c.c. was poured off, and the loss of methyl-blue determined in the colorimeter of Lummer and Brodhun by comparison with 100 c.c. of standard solution. In the case of a large proportion of oxycellulose, this would have to be diluted from 0·25 to 1·125 per cent.

One grm. pure cellulose fixed 0·0012 grm. methyl-blue. The products of the experiments of Table III. gave the following results:—

TABLE X.

Experiment.	Methyl-blue fixed by 1 grm. substance.
	Grm.
1.	0·0010
2.	0·0009
3.	0·0011
6.	0·0021
8.	0·0036
11.	0·0120

According to these experiments, no formation of oxycellulose would occur in nitration with concentrated acid mixtures, as the products obtained in comparison with cellulose show no increased affinity for methyl-blue. The latter is therefore not changed by introducing NO_2 groups into the cellulose molecule; accordingly the increase of this capacity in using dilute acid mixtures is entirely due to secondary action in the mixture, viz., to the formation of oxycellulose.

A similar phenomenon was observed in the products of the last-named series of experiments. By increasing addition of sulphuric acid to nitric acid 1·4, the affinity of the resulting products for methyl-blue is increased; it reaches a maximum (fixing by 0·0123 grm.) in a nitration mixture with 26 per cent water, and then diminishes again on further concentration of the nitration mixture by addition of sulphuric acid.

The products obtainable with dilute acid mixtures are therefore to be regarded as nitro-oxycelluloses, *i.e.*, mixtures of nitrocelluloses with nitro-oxycelluloses.

This has recently been demonstrated from another direction. According to Dr. Brönnert, and also Leo Vignon, a formation of oxycellulose should also take place in concentrated acid mixtures, which is a contradiction of our experiments. Vignon determined the reducing power of his products against Fehling's solution, and found it approximately equally great with nitrated cellulose as with nitrated oxycellulose. Hence the reducing action does not run parallel with the affinity for basic colour stuffs, and it is therefore scarcely probable that these two phenomena are both due to the same cause—the presence of oxycellulose. By treating our own products, given in Table X., with Schiff's reagent (a fuchsine solution rendered colourless with sulphuric acid) it is seen that the intensity of the red colouration, which is due to the presence of aldehyde groups, increased in a similar manner as the affinity for methyl-blue. These merely qualitative experiments indicate that the formation of aldehyde groups in concentrated acid mixtures is very slight, but that it increases with the dilution of the nitration acids, like the methyl-blue reaction.

If, now, the reducing power of the products depended entirely on the presence of aldehyde groups, it should vary in different nitration mixtures in the same manner as the above reactions. But as Vignon has found no difference, the reducing power cannot stand in a direct relation to the aldehyde groups, *i.e.*, to the oxycellulose. We must therefore adhere to our conclusion that, in using concentrated acid mixtures, there is practically no formation of oxycellulose.

(To be continued).

AN IMPROVED METHOD OF PRODUCING ULTRA-VIOLET-SENSITIVE PLATES.*

By V. SCHUMANN.

(Concluded from p. 68).

The Original and the Improved Method.—My method published in 1893 consisted in diluting with much water an emulsion poor in gelatin, and pouring it into basins in which the silver haloid was deposited from a thick layer upon glass plates laid inside. After the formation of the sensitive film, for which several hours were required, the emulsion was poured off, and the plates dried horizontally.

From this it is obvious that the two methods, the old and the improved, are very similar, but it would be a mistake to judge thus of the photographic nature of their plates; for the two have no more in common than their sensitiveness to ultra-violet rays, the rapid fixing and drying, and their behaviour towards potassium iodide in the developer. In their remaining characteristics they differ widely from each other.

The most striking is their relation to silver iodide. While the emulsion of the older process could stand a considerable quantity of silver iodide, the improved plate becomes fogged in its presence to the extent of being quite useless. All efforts to introduce silver iodide into the sensitive film are frustrated by the easy reduction and excessive intensity which it imparts. I have, nevertheless, after many vain attempts, made it yield to a standing development of seven hours' duration, and obtained negatives tolerably free from fogging, but it is clear that so lengthy a developing process is of no service to spectroscopy.

The improved method depends far more upon the character of the gelatin than does the older. A certain kind of gelatin, used formerly with success, now led to a series of strange irregularities. Besides a variety of spots, the film thus prepared exhibited in the wet condition, a few minutes after pouring off the emulsion, a number of cracks, about 2¼ c.m. long, shaped like the tail of a comet, which made the plate useless. In another case one of our best German emulsion-gelatins gave such feebly sensitive films that it was not even possible to reproduce the wave-length 185 $\mu\mu$, which may be easily done even with the ordinary gelatin plate. But the plate completely changed its character after remaining ten minutes in a bath of warm water (38° C.), thus attaining to a surprisingly high degree of sensitiveness towards ultra-violet rays. In this case the water plays the part of a physical sensitising agent. Its sensitising action depends upon setting free the upper part of the sensitive film from its light-absorbing outer layer, and also increasing the reducing capacity of the silver bromide by warming. The sensitising action of this water-bath upon this kind of plate exceeds every experience that I have had in my years of working with ultra-violet sensitive preparations. Unfortunately the bath causes spots and drying zones of varying sensibility, so that plates of this kind cannot be recommended, all the less so that the sensitising in the bath imperils the stability of the plate.

Of the different kinds of gelatin that I have tried, one only gave permanently good films—that is the soft gelatin already mentioned of English origin that comes into the market under the trade mark Nelson No. I., known in photographic circles. Therefore I should like to advise all who wish to prepare these plates to use this gelatin and no other.

The older plate was treated with weak developer, the improved plate, on the other hand, may be treated with a solution of unusual strength, more especially not long after preparation of the plate. But, before all things, it is more reliable and more uniformly sensitive, becoming so

* *Annalen der Physik*, 1901, vol. v.

in the process in which the coarser silver bromide particles are removed from the film during deposition.

The capacity for decomposition of rays is one of the sensitive plate makes it highly advantageous to the reproductions of dense groups of lines of large energy differences. My older attempts leave something to be desired in this direction, for in them the lines frequently spread themselves into an indissoluble surface, in which only the most marked lines could be distinguished. This objection, which is entirely due to a lack of half-tones, is obviated in the improved method by the delicate gradation of its negative.

I have already alluded to the action of potassium iodide in the developer of ultra-violet plates. I found that a few drops of a solution of 1:100 accelerated the appearance of the image, but also easily induced fogging, which, in distinction to the fogging of other plates, did not appear simultaneously over the whole film, but spread slowly from the edges to the middle. I have now attempted to utilise this accelerating action of potassium iodide for the improved plate, by immersing it before exposure for a few minutes in dilute solutions of potassium iodide, and then allowing it to dry. The result did not answer my expectation, for the former objections were again apparent.

Use of the Improved Plate in Spectroscopy.—The ultra-violet plate excels all others in giving faithful reproductions of the whole photographic energy of the source of light, from blue to the shortest wave-lengths, while the gelatin dry plate takes the precedence whenever the region lying beyond 220 $\mu\mu$ is not to be taken into consideration.

The sensitiveness of the ultra-violet plate first becomes marked at 220 $\mu\mu$, and increases with the refrangibility of the rays to a high degree.

The gelatin dry plate fails at 182 $\mu\mu$. It is still slightly sensitive towards the shorter waves, but it gives unreliable spectra of these, because in every case, owing to the absorption action of the gelatin, it develops as a white continuous band, and does not give the energy difference of the different waves. Hence, the ultra-violet plate is alone suitable to the photography of the spectrum beyond 182 $\mu\mu$.

THE DETERMINATION OF PHOSPHATES IN POTABLE WATERS.*

By A. G. WOODMAN and L. L. CAYVAN.

(Concluded from p. 71).

The Effect of Silica.

The properties of dilute solutions of ammonium silico-molybdate were also studied, since silica is the principal substance which interferes with the phosphate test.

Solutions made up with varying quantities of the standard silica solution gave a colour immediately upon adding the reagents. With small and medium amounts of silica the colour was slight compared with that developed in an hour; with high silica standards considerable colour developed instantly. It is interesting to note that ammonium molybdate alone with a silica solution made exactly neutral, develops a faint colour in an hour, but with a phosphate standard no colour appears except in the presence of nitric acid. In twenty-four hours the colour due to the silico-molybdate fades appreciably; it is greener than the colour of the phospho-molybdate.

To determine the time necessary for silica standards to attain their maximum colour, varying standards were mixed with the reagents and 50 c.c. of water and compared at definite intervals with fresh phosphate standards. The readings in terms of the standard phosphate solution are given in the following table:—

C.c. SiO_2 used.	½ hour.	1 hour.	1·5 hours.	2·5 hours.	3 hours.	3·5 hours.
0·1	0·03	0·07	0·09	0·03	0·02	0·03
0·7	0·56	0·65	0·67	0·72	0·70	0·67
1·0	0·92	0·96	1·01	1·02	1·07	1·05
3·0	2·75	2·88	2·95	3·01	2·95	2·95
7·0	6·65	6·75	6·95	7·00	7·10	7·20
10·0	9·70	9·95	9·99	9·95	9·95	—

C.c. SiO_2 used.	4·5 hours.	5 hours.	5·5 hours.	6 hours.	6·5 hours.	7 hours.
0·1	0·02	0·01	0·01	0·01	0·008	0·008
0·7	0·67	0·67	0·66	0·66	0·65	0·65
1·0	1·05	1·04	1·03	1·03	1·02	1·02
3·0	3·10	3·20	3·20	3·25	3·30	3·40
7·0	7·20	7 20	7·25	7·25	7·30	7·35
10·0	9·95	9·95	9·95	9·95	9·95	9·90

It will be noticed that the lower standards reach a maximum in about two or three hours, and then begin to fade; the medium standards do not seem to reach a maximum even after seven hours.

A number of silica standards, after standing one hour, were heated from 20° to 100° in a water-bath. The colour did not change in intensity until 70—80° was reached, when it began to fade, decreasing up to 100°. The colour did not return to its original intensity on cooling slowly to 20°.

Experiments made to determine the conditions under which minute quantities of silica might be rendered entirely insoluble showed that evaporation with nitric acid and heating at 100° for an hour was insufficient; when the same standards were evaporated and heated at 135° for an hour, re-combination took place and some of the silica remained soluble. On heating the residues for *two* hours at 100° instead of one hour, however, no silica remained soluble. The results are shown in the following table. 1, 2, and 5 c.c. of the standard silica solution were diluted to 50 c.c., 10 drops of nitric acid were added, the solutions evaporated to dryness in porcelain dishes, and heated at different temperatures for two hours. The residue was taken up in cold water and the colour read after standing one hour:—

Temperature.	Readings.			Per cent undehydrated SiO_2.		
	1 c.c.	2 c.c.	5 c.c.	1 c.c.	2 c.c.	5 c.c.
60°	0·5	1·2	2·0	50	60	40
80°	0·3	0·7	0·9	30	35	18
100°	0·0	0·0	0 0	00	00	00
135°	0·1	0·4	1·0	10	20	20
150°	0·4	0·5	1·1	40	25	22
190°	0·6	0·8	1·1	60	40	22

Other Compounds which might Interfere.

Since vanadium and titanium resemble phosphorus and silicon quite closely in many of their properties, vanadates and titanates might interfere with the determination of phosphates by a colorimetric method. Titanium is especially liable to occur in the natural waters of regions containing diorites and titanium-bearing ores like ilmenite. The presence of these elements has been observed in natural waters.

Dilute solutions of sodium titanate gave a pale greenish yellow colour with ammonium molybdate and nitric acid, but much less intense than the phosphate colour. The colour did not fade within an hour, but at 20° C. it took twelve minutes for it to appear. By evaporation with nitric acid, and subsequent heating at 100° for two hours, the titanium oxide was rendered completely insoluble.

Ammonium vanadate gave with the ammonium molybdate *alone* a yellow colour which was permanent for several hours, but upon the addition of nitric acid this colour faded completely in five minutes. Experiments with a standard solution of ammonium vanadate showed that the colour given by as much as 0·0003 grm. of V_2O_3 in 50 c.c. of water fades out entirely in four minutes. Incidentally it was found that 0·000001 grm. of V_2O_3

* Contributions from the Laboratories of the Massachusetts Institute of Technology. From the *Journal of the American Chemical Society*, xxiii., No. 2.

could be detected readily in a volume of 50 c.c. It is evident that the small quantities of vanadium which occur in natural waters will not interfere with the determination of phosphates.

Colorimetric Estimation of Phosphates in the presence of Silica.

The previous results had shown the possibility of a method based on the dehydration and elimination of the silica. The conditions must be such that the total phosphate or a definite portion of it shall be left intact and that the silica shall be rendered entirely insoluble. The following method was finally adopted as the one giving the most satisfactory results:—

Fifty c.c. of the water and 3 c.c. of nitric acid (sp. gr. 1·07) are evaporated to dryness in a 3-inch porcelain dish on a water-bath. The residue is heated in an oven for two hours at the temperature of boiling water. The dry residue is then treated with 50 c.c. of cold distilled water, added in several portions, and poured into the comparison tube. It is not necessary to filter the solution. Four c.c. of ammonium molybdate and 2 c.c. of nitric acid are added, the contents of the tube mixed, and the colour compared after three minutes with standards made by diluting varying quantities of the standard phosphate solution to 50 c.c. and adding the reagents as above. A blank should always be made on the distilled water used for dilution, especially if it has stood for any length of time in glass vessels.

The method as just described will be sufficient for ordinary work. If a more exact determination of the phosphate is required, a slight correction should be applied in each case. These corrections were determined by making a number of determinations by the method. The results are shown in the following table. The first two series had two c.c. of standard silica solution added to each test; the others had only the phosphate:—

Phosphate added.	Phosphate found.						Average.	Correction.
0·1	0·07	0·09	0·10	0·10	0·09	0·09	0·09	0·01
0·5	0·46	0·47	0·46	0·45	0·43	0·45	0·45	0·05
0·7	0·63	0·64	0·64	0·65	0·64	0·66	0·65	0·05
1·0	0·85	0·85	0·86	0·86	0·84	0·83	0·85	0·15
3·0	2·55	2·65	2·50	2·50	2·60	3·65	2·60	0·40
5·0	4·55	4·55	4·45	4·45	4·50	4·50	4·50	0·50
7·0	6·65	6·60	6·55	6·55	6·60	6·65	6·60	0·40
10·0	9·60	9·65	9·55	9·60	9·60	9·55	9·60	0·40

Since organic life is present in greater numbers and is more active in surface waters than in ground waters it is evident that the determination will be of greatest value for the examination of wells. Well-waters are usually colourless, and to them the method may be applied directly. It is not yet suitable for coloured waters. The determination of phosphates is at present being carried on in this laboratory as a routine determination, and the results will be published as soon as sufficient data have accumulated to render a discussion of the entire question of value.

COMPOUNDS OF METHYL SULPHIDE WITH HALIDES OF METALS.*

By FRANCIS C. PHILLIPS.

(Concluded from p. 69).

Compound of Methyl Sulphide with Cuprous Chloride.

WHEN methyl sulphide is added to a concentrated solution of cupric chloride, the colour of the liquid changes from green to dark brown, and heat is evolved. After standing for a few hours, a mass of white crystalline scales forms at the bottom. The compound, if rapidly washed and dried, is white, but it is liable to turn to a yellowish green during drying. Exclusion of air does not serve completely to prevent this change of colour. The crystals are almost insoluble in water, and are very slightly soluble in the various organic liquids mentioned in connection with the mercury compound. Boiling with water seems to expel part of the methyl sulphide. The substance dissolves in ammonia and in nitric acid.

Caustic alkalis decompose it, yielding an insoluble brownish red powder. Digestion of the substance with hydrogen sulphide gradually changes it to copper sulphide. This reaction was made use of for a determination of the copper, the sulphide being ignited, re-dissolved, precipitated by sodium hydroxide, and weighed as cupric oxide. Chlorine was determined in the filtrate from the copper sulphide by the method already mentioned. As there seemed to be a possibility that the chlorine might be linked to carbon rather than to copper, and that consequently it might not be fully set free as hydrochloric acid in decomposing the compound by hydrogen sulphide, determinations were also made by heating the substance in a combustion tube traversed by a stream of hydrogen, absorption of the hydrogen chloride produced in water, neutralisation by zinc, and titration by silver nitrate solution. Determinations were also made by decomposition of the copper chloride compound by magnesium powder and titration of the chlorine as magnesium chloride. Sulphur was determined by the method of combustion in oxygen already described. The results of analysis were as follows:—

	Per cent.	
Copper	39·12	
	39·13	
Chlorine	21·85	Decomposition of the compound by hydrogen sulphide.
	21·80	
	21·76	Decomposition by magnesum.
	21·77	
	21·76	Decomposition by heating in hydrogen.
	21·60	
Sulphur	19·62	
	19·70	

The calculated percentages of the constituents named in the case of a compound having the composition $CuCl(CH_3)_2S$ are:—

	Per cent
Copper	39·46
Chlorine	22·00
Sulphur	19·90

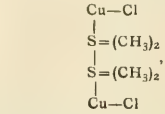
Cuprous chloride methyl sulphide heated in nitrogen gives off methyl sulphide at about 100° C., and continues to lose methyl sulphide until the temperature reaches about 200° C. After heating to a somewhat higher temperature the chlorine present in the residue in one experiment was found to amount to 21·53 per cent of the original weight of the portion of the compound employed.

At a temperature above 400° the compound yields a mixture of copper sulphide and copper in wire form. The reaction occurring between methyl sulphide and the solution of cupric chloride which leads to the formation of the compound $CuCl(CH_3)_2S$, is characterised by great intensity, as evidenced by the heat evolved and by the promptness of the change. One-half of the chlorine in the cupric chloride is eliminated, and in its stead methyl sulphide becomes linked to the copper. Apparently, therefore, the substance resulting should be a cupric compound. Judged by its white colour and its chemical properties it is, apparently, to be classed as a cuprous and not as a cupric compound. Yet it does not seem probable that the copper atoms can be in this case linked as is supposed to be the case in cuprous chloride,

$$\begin{matrix} Cu—Cl \\ | \\ Cu—Cl \end{matrix}.$$

The constitution of the compound might perhaps be expressed by the formula,

* *Journal of the American Chemical Society*, vol. xxiii., No. 4.



in which the sulphur appears to be tetravalent. The copper atom is no doubt linked more firmly to the chlorine than to the sulphur of the methyl sulphide. The question as to the classification of the compound as cuprous or cupric, seems to depend merely on whether there are one or two carbon atoms linked to the copper atom. The linking of a chlorine atom, together with the sulphur atom of a methyl sulphide group to a copper atom, seems to impart to the compound a cuprous character, as if the chlorine atom alone were present.

Compound of Methyl Sulphide with Gold Chloride.

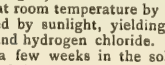
When methyl sulphide is added to a solution of auric chloride, much heat is evolved, and an escape of hydrogen chloride occurs, while an apparently flocculent white precipitate is produced. This precipitate is insoluble in water, but slightly soluble in alcohol. It may be washed and dried at room temperature by gas-light. It is rapidly decomposed by sunlight, yielding metallic gold, methyl sulphide, and hydrogen chloride. If preserved in a dark place for a few weeks in the solution in which it was formed, and in presence of a slight excess of methyl sulphide, it assumes the shape of colourless crystalline needles.

It dissolves in various organic liquids, but the solutions soon deposit metallic gold. A determination of gold was made by exposing the substance under water to direct sunlight. The gold was rapidly reduced, and was filtered out, burnt, and weighed in the metallic state. The chlorine was determined volumetrically in the filtrate from the gold. The sulphur was determined by combustion in oxygen, and weighing as barium sulphate.

The following analytical results were obtained:—

	Per cent.
Gold	67·16
	66·98
	66·77
	67·42
Chlorine	12·32
	12·35
	11·97
	11·74
Sulphur	10·99
	10·88

These results suggest the composition—



since calculation shows that such a compound would contain:—

	Per cent.
Gold	66·90
Chlorine	12·02
Sulphur	10·87

The gold compound was heated in nitrogen, when it was found that an evolution of methyl sulphide begins at about 100°, and continues until the temperature approaches 200°. At higher temperature, pure gold is left as a residue.

The reaction leading to the formation of the gold compound resembles that by which the copper compound is produced, in that the auric chloride undergoes reduction, and the aurous chloride then unites with methyl sulphide. A trivalent gold atom appears to have its affinities satisfied partly by a chlorine atom, and partly by the sulphur atom of a methyl sulphide group.

It seems that in the compounds which have been here mentioned the metal is more firmly linked to the halogen than to the sulphur of the methyl sulphide, and that the part played by the methyl sulphide is somewhat like that of water in various hydrated salts. Ferrous chloride remains a ferrous compound no matter what may be the number of water molecules with which it combines.

Hydrated magnesium chloride is well known to lose hydrochloric acid on strong heating, and in a somewhat analogous fashion some of the compounds of metallic halides with methyl sulphide decompose on heating into metallic sulphide and methyl chloride.

A further study of compounds of alkyl sulphide with other metallic halides is in hand.

My acknowledgments are due to Mr. J. C. Fetterman, assistant in this laboratory, for his skill and careful attention to details in conducting many difficult and somewhat tedious analyses in connection with this work.

THE ESTIMATION OF CARBONIC ACID IN WATER.*

By JOSEPH W. ELLMS and JAY C. BENEKER.

THE estimation of carbonic acid is of considerable importance in the technical analysis of water. In the softening of water for manufacturing purposes and in the purification of public water supplies, where certain processes are employed, an accurate knowledge of the amount of this constituent is essential to a proper treatment of the water. Moreover, in the sanitary analysis of sewage, of effluents from sewage purification plants, and of polluted waters generally, a determination of the amount of carbonic acid present may throw considerable light on the nature and extent of the chemical and bacterial changes which are taking place.

Condition in which Carbonic Acid exists in Natural Waters.

Before discussing the methods usually employed for the estimation of carbon dioxide in water, and the principles upon which these methods are based, it may be well to consider in what forms of combination carbon dioxide exists in water, and to define the different terms which are used to designate them.

The carbonates which are commonly found in natural waters are those of calcium and magnesium. The normal carbonates of these bases are, relatively speaking, but sparingly soluble in water. If, however, more than enough carbon dioxide be present to unite with the oxides of calcium and magnesium to form the compounds $CaCO_3$ and $MgCO_3$, the solubility of these salts is much increased. It is generally assumed, that when there is present one extra molecule of carbon dioxide for each molecule of calcium carbonate or of magnesium carbonate, compounds of the character of sodium bicarbonate exist, although such salts have never been isolated. These salts are presumed to have the composition represented by the formulæ $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$, respectively.

The gas carbon dioxide (CO_2) is quite soluble in water, and therefore may exist in natural waters in amounts greater than is required to form the bicarbonates of the alkaline earth bases which may be present. It is usually considered that carbon dioxide thus dissolved in the water exists as a true acid having the formula H_2CO_3.

From the above it is evident that there are three conditions in which carbon dioxide may be present in natural waters. If the carbon dioxide is not combined with any base, it is spoken of as "free carbonic acid"; if it is combined indirectly with the base as in the form of the bicarbonates, it is termed "half-bound carbonic acid"; and if directly united to the bases as in calcium and magnesium carbonates, it is called "fixed carbonic acid." The sum of the amounts of the carbonic acid found in these three forms is usually spoken of as the "total

* *Journal of the American Chemical Society*, xxiii., No. 6.

carbonic acid." The carbonic acid that is expelled on heating aqueous solutions containing either "free" or "half-bound carbonic acid," or both, is sometimes spoken of as "volatile carbonic acid."

Natural waters carry varying amounts of carbonic acid, depending on the character of the geological formations with which they have come in contact. Ground waters having probably been under greater pressure usually contain more carbonic acid than surface waters. Moreover, ground waters which become exposed to the air lose the larger proportion of their free carbonic acid, and may even part with some of their half-bound and fixed carbonic acid. The loss of the latter results, of course, from a precipitation of carbonates (calcium carbonate principally), as a result of the loss of some of the half-bound carbonic acid.

It was found that the ordinary distilled water of the laboratory might contain from six to ten parts per million of free carbonic acid. It was necessary to boil off 10 to 15 per cent of the original volume of such a water in order to free it completely from the gas. A water thus freed from carbonic acid absorbs, when exposed to the air, more or less carbon dioxide depending on the amount present, and on the temperature and pressure. Two samples of distilled water free from carbonic acid were exposed in beakers to the air of the laboratory in which the temperature was approximately 16° C.

	A. Free carbonic acid. Parts per million.	B. Free carbonic acid. Parts per million.
Original water	0	0
After twenty-four hours ..	2·2	2·2
After forty-eight hours ..	15·0	13·2
After seventy-two hours ..	0·9	0·9

The great variation in the amounts obtained was probably due to the differing quantities of carbonic acid present in the atmosphere of the laboratory on the particular day the samples were examined. On the second day a carbonic acid generator was being used in the laboratory, and considerable gas was also being burned.

Waters containing large amounts of calcium bicarbonate and free carbonic acid, not only lose their free but also a portion of their half-bound carbonic acid, when exposed to the air for any length of time. The excess of calcium carbonate ($CaCO_3$) is thereby precipitated, and the solution grows weaker in lime, until a state of equilibrium is reached.

The following experiments illustrate the action of a strong solution of calcium bicarbonate ($Ca(HCO_3)_2$), when exposed to the air of the laboratory:—

	A. Carbonic acid in solution. Parts per million.			B. Carbonic acid in solution. Parts per million.		
	Free.	Half-bound.	Fixed.	Free.	Half-bound.	Fixed.
Original water	52·8	109·4	109·4	52·8	109·4	109·4
After 24 hours	7·9	—	—	7·0	—	—
After 48 hours	1·3	—	—	1·1	—	—
After 72 hours	0	80·7	84·5	0	80·7	84·5

Magnesium bicarbonate is much more soluble in water than calcium bicarbonate, but strong solutions show the same tendency to give up their half-bound carbonic acid as do strong solutions of calcium bicarbonate. This occurs, however, without any precipitation of magnesium carbonate ($MgCO_3$) because the latter itself is quite soluble in water.

A strong solution of magnesium bicarbonate lost all of its free and 12 per cent of its half-bound carbonic acid in less than three days when exposed to the air of the laboratory. This solution, therefore, contained 12 per cent of its total magnesium carbonate in the form of normal magnesium carbonate ($MgCO_3$). On the other hand, the calcium bicarbonate solution, as shown above, contains only 4 per cent of its total calcium carbonate in the form of the normal carbonate ($CaCO_3$). This illustrates the difference in degree of the affinity of solutions of these two salts for carbon dioxide.

However, solutions of calcium and magnesium carbonate which contain no half-bound or free carbonic acid, or only very limited amounts of the former, tend to absorb the gas from the air, and thus form the bicarbonates of these bases. Calcium carbonate solutions in time become acid (*i.e.*, contain free carbonic acid), but the acidity is always very slight, and the state of equilibrium seems to be reached when the lime is all in the form of the bicarbonate. On the contrary, weak solutions of magnesium carbonate, while they absorb carbon dioxide from the air to form magnesium bicarbonate, only very slowly approach the condition where all the magnesium exists as bicarbonate; in fact the tendency seems to be for the solution to remain as a mixture of these two compounds. That these facts have a bearing on certain classes of natural waters will be shown later.

Principles on which Methods for the Estimation of Carbonic Acid are Based, with a Discussion of the Errors Affecting their Accuracy.

A comparison of the three most commonly employed volumetric methods for the determination of carbonic acid in water has been made by the writers, with the purpose of discovering, if possible, the sources of error which affected each of them, and also to learn which gave results closest to amounts actually known to be present in solution.

The oldest and best known of the three methods was suggested by Pettenkofer (*N. Rep. Pharm.*, x., i.). Trillich (*Ztschr. Angew. Chem.*, June 15, 1889, p. 337) modified this method in order to avoid certain difficulties arising in the original method, and as this modification is quite radical, the process as carried out by him can be considered practically as a new method. Seyler (CHEM. NEWS, lxx., 1894, 104; and *Analyst*, 1897, xxii., 312), advocates what he terms the Lunge-Trillich method, which in principle differs materially from that of Pettenkofer's or Trillich's modification of Pettenkofer's method.

These three methods were those which were investigated and compared. In order to avoid confusion the three will be designated in this paper as Pettenkofer's, Trillich's, and Seyler's methods respectively.

(To be continued).

ON THE METEORIC STONES WHICH FELL NEAR ZOMBA, BRITISH CENTRAL AFRICA, ON JANUARY 25TH, 1899. WITH NOTES ON THE CHEMICAL ANALYSIS OF SUCH BODIES.*

By L. FLETCHER, M.A., F.G.S.,
Keeper of Minerals in the British Museum.

(Continued from p. 66).

Specific Gravity of the Zomba Enstatite.

29. SINCE the proportions by weight of the three constituents of the undecomposed material and the specific gravities of two of them (felspar and chromite) are known, it is now possible from the specific gravity of the mixture (§ 14) to calculate the specific gravity of the third constituent (enstatite). The specific gravity of oligoclase, Ab_3An_1, is 2·66; that of chromite varies from 4·32 to 4·57 (Dana), the mean of which is 4·44; that of the mixture was found to be 3·171 (§ 14). The total volume of a mixture being the sum of the volumes of the constituents, it follows that, if x be the specific gravity of the enstatite,—

$$\frac{78\cdot71}{x} + \frac{19\cdot84}{2\cdot66} + \frac{1\cdot45}{4\cdot44} = \frac{100}{3\cdot171}.$$

Whence x is 3·314.

* From the *Mineralogical Magazine*, vol. xiii., No. 59, 1901.

The specific gravity of the Lodran enstatite was directly determined by Professor Tschermak to be 3·313.

Undecomposed Material: Amount of Action of Hydrochloric Acid and Sodic Solution.

30. The trace of undecomposed material, which, after treatment with hydrofluoric and sulphuric acids, weighed 0·0014 (§ 17), must before that treatment have weighed 0·0017 (§ 19); hence SiO_2 is 0·0746; and the total amount of undecomposed silicate is 0·0017+0·8807+0·0363 or 0·9187; for ignition does not appreciably alter the weight of the undecomposed material (§ 18). After deduction of SiO_2 0·0049 due to the sodic solution itself (§ 13), we have, for the SiO_2 due to the silicate, 0·0697.

For the hydrochloric acid extract:—

Fe_2O_3,Al_2O_3,SiO_2 0·0150 consisted of Fe_2O_3 0·0140 (corresponding to FeO 0·0127), Al_2O_3 0·0009, SiO_2 nil.

Deducting 0·0054 from $Mg_2P_2O_7$ 0·0649 as being really $Ca_2P_2O_7$ due to the action of the nitric acid on the porcelain (§ 20), we have $Mg_2P_2O_7$ 0·0595, corresponding to MgO 0·0215. Collecting the results:—

	Acid extract.	Sodic extract.	Total extract.
SiO_2	—	0·0697	0·0697
FeO	0·0127	—	0·0127
MnO	—	—	—
MgO	0·0215	—	0·0215
CaO	0·0076	0·0023	0·0099
Al_2O_3	0·0009	0·0062	0·0071
K_2O	Undet.	Undet.	Undet.
Na_2O			
Total extract			0·1209
Undecomposed residue			0·9187
Weight found			1·0396
Weight taken			1·0388

Hence it follows that when the undecomposed material is subjected to the action of hydrochloric acid and sodic solution in the same way and for the same length of time as in the analysis of the mixed powder itself, no less than 11·64 per cent pass into the acid or sodic solution. As there is little alumina in the acid extract, either the felspar is only very slightly attacked by the acid, or the alumina is set free in such a form as to be only with difficulty soluble in the acid, though removable by the sodic solution (*Journ. Chem. Soc.*, 1882, vol. xli.; *Transactions*, p. 159); more probably the greater part of the decomposition of the felspar is due to the sodic solution itself.

If we allow soda in sufficient proportion to form oligoclase with the alumina (§ 24) the percentage composition of the total extract is—

SiO_2	56·44
FeO	10·29
MnO	—
MgO	17·41
CaO	8·02
Al_2O_3	5·75
K_2O	2·09
Na_2O	
	100·00

The total extract has thus nearly the same composition as the original mixture (§ 23). The chief part of the solvent action on the enstatite is due to the acid; the silica set free by this action is removed by the sodic solution, which at the same time acts to some extent on the felspar, taking all the constituents into solution, and probably to some extent on the enstatite, removing the silica and lime but leaving its oxide of iron and magnesia in the final residue. The corresponding oxide of iron and magnesia left in the undecomposed residue by the action of the previous sodic solution will have passed into the acid extract.

Unattracted Material: Treatment with Mercuric Solution.

31. Fe_2O_3 0·0021 (§ 9) corresponds to Fe 0·0015. Hence the total amount of alloy extracted by the mercuric solution from 4·9856 grms. of the unattracted material was at most 0·0022, containing 31·82 per cent of nickel; as already stated, the high percentage of the nickel was already manifested by the colour of the extract. This again points to the easy oxidation of the iron of the finer particles of nickel-iron during the exposure to the air in the course of the magnetic separation and afterwards; the nickel being less easily oxidised and less readily attracted by the magnet, the percentage of the nickel in the metallic portion still left with the unattracted material will be higher than in the original nickel-iron.

Unattracted Material: Alkalis.

32. K_2PtCl_6 0·0040 (§ 8) corresponds to KCl 0·0012; 0·0036, adherent to the filter and ignited, if taken as Pt_2KCl, corresponds to KCl 0·0016; making altogether KCl 0·0028.

From the blank experiment (§ 22) the KCl due to the reagents is 0·0021; hence only KCl 0·0007 can be assigned to the silicate.

The mixed chlorides due to the silicate weigh 0·0135 (§ 8)−0·0021 (§ 22), or 0·0114; the NaCl is thus 0·0107.

These amounts of NaCl and KCl correspond respectively to Na_2O 0·0057 and K_2O 0·0004 for 0·4815 of material, and to Na_2O 1·18 and K_2O 0·08 per cent.

As the total amount of matter extracted from the unattracted material by boiling water amounted to only 0·26 per cent, and part of it consisted of calcium and magnesium, it is inferred that the alkalis were present in the unattracted material as constituents of an insoluble compound, presumably felspar.

Unattracted Material: First Portion.

33. The trace of undecomposed material which, after treatment with hydrofluoric and sulphuric acids weighed 0·0039 (§ 10), must before that treatment have weighed 0·0047 (§ 19); and the total amount of undecomposed material is 0·0047+0·9186+0·1328 or 1·0561, for ignition does not appreciably alter the weight of undecomposed material (§ 18).

The true SiO_2 is 0·4909−0·0047 or 0·4862; but of this 0·0049 are due to the sodic solution itself (§ 13); the SiO_2 really due to the silicate is thus 0·4813. Of the Fe_2O_3,Al_2O_3,SiO_2 0·0048, the Fe_2O_3 was small, and probably only that from the sodic solution itself, 0·0009 (§ 13); the SiO_2 was 0·0031 (making the total SiO_2 0·4844) and (by deficit) Al_2O_3 is 0·0008.

The Fe_2O_3,Al_2O_3,SiO_2 0·4639 from the acid extract consists of Fe_2O_3 0·4578 (corresponding to FeO 0·4120), Al_2O_3 0·0040 (and SiO_2 0·0021 due to the action on the vessels).

Further, 2·5065 of unattracted material contains an amount of sulphur (§ 7) corresponding to FeS (troilite) 0·1412, which is itself equivalent to FeO 0·1155; as this iron is in the acid extract, only FeO 0·2965 (*i.e.*, 0·4120−0·1155) is due to the silicate.

MnS 0·0068 corresponds to MnO 0·0055.

(NiO 0·0001 may be neglected in the calculations).

Hence we have—

		Percentages.
Undecomposed material	1·0561	42·13
Troilite	0·1412	5·63
SiO_2	0·4844	19·33
FeO	0·2965	11·83
MnO	0·0055	0·22
MgO	Undet.	Undet.
CaO	Undet.	Undet.
Al_2O_3 {Acid extract 0·0040 / Sodic extract 0·0008} ..	0·0048	0·19
K_2O	Undet.	Undet.
Na_2O	Undet.	Undet.
Total	1·9885	79·33
Weight taken ..	2·5065	100·00

Unattracted Material: Second Portion.

34. The amount of volatile material corresponding to 2·7333 of the material taken for analysis would be 0·0680 (§ 11), and the weight of the pure material was thus 2·6653.

The trace of undecomposed material which, after treatment with hydrofluoric and sulphuric acids, weighed 0·0017 (§ 11), must, before that treatment, have weighed 0·0021 (§ 19); and the total amount of undecomposed material is 0·0021+1·0981+0·0516, or 1·1518, for the weight of the undecomposed material is not appreciably altered by the ignition (§ 18).

The true SiO_2 is thus 0·5296−0·0021 or 0·5275; but of this, 0·0049 is due to the sodic solution itself (§ 13); the SiO_2 really due to the silicate being therefore 0·5226.

The Fe_2O_3,Al_2O_3,SiO_2 0·0065 consists of Fe_2O_3 0·0020, Al_2O_3 0·0035, and SiO_2 0·0010 (making the total SiO_2 0·5236); deducting Fe_2O_3 0·0009 as due to the sodic solution itself, Fe_2O_3 0·0011 has passed into the sodic solution from the silicate (possibly through finely-divided silicate passing through the pores of the filter).

The Fe_2O_3,Al_2O_3,SiO_2 0·5013 of the acid extract consists of Fe_2O_3 0·4960, Al_2O_3 0·0019, and SiO_2 0·0034 (due to action on the vessels).

(NiS ignited 0·0012 may be omitted in the calculations).

MnS 0·0074 corresponds to MnO 0·0060.

The $Mg_2P_2O_7$ (pure) is 1·3834 (§ 11)−0·0054 (§ 20) or 1·3780, corresponding to MgO 0·4989.

The total Fe_2O_3 is 0·4960+0·0011 or 0·4971, corresponding to FeO 0·4474; further, 2·6653 of the unattracted material contain an amount of sulphur (§ 7) corresponding to FeS (troilite) 0·1502, which itself is equivalent to FeO 0·1259; as this iron is in the acid extract, only 0·3215 (*i.e.*, 0·4474−0·1259) of FeO is due to the silicate.

The total CaO obtained is 0·0013+0·0105 or 0·0118; from this must be deducted 0·0005 as due to the sodic solution (§ 13).

Also 2·6653 of the unattracted material contains (§ 22) K_2O 0·0022, Na_2O 0·0315; and the 1·1518 of undecomposed material contain (§ 22) K_2O 0·0021, Na_2O 0·0182; hence there must have passed into the acid and alkaline solutions K_2O 0·0001 (or nil) and Na_2O 0·0133.

Collecting the results we have:—

		Percentages.
Undecomposed material	1·1518	43·21
Troilite	0·1502	5·64
SiO_2	0·5236	19·65
FeO	0·3215	12·06
MnO	0·0060	0·23
MgO	0·4989	18·72
CaO	0·0113	0·42
Al_2O_3 { Acid extract 0·0019 / Sodic extract 0·0035 }	0·0054	0·20
K_2O	Nil	Nil
Na_2O	0·0133	0·50
Total	2·6820	100·63
Weight taken	2·6653	100·00

(To be continued).

ON NITROMETER WORK.

By C. H. SHEPARD.

The following work was done on the usual nitrometer, composed of a decomposing bulb and reservoir, and the complement of a measuring tube, reduction tube, and reservoir. The measuring tube had a capacity of 140 c.c. The potassium nitrate used was Merck's, chemically pure, re-crystallised. About 0·5 grm. was used for each determination. The temperature of the laboratory, while the work was being done, was approximately 68° F. The dry potassium nitrate was weighed out into tared weighing-bottles, and about 15 c.c. of sulphuric acid added. The bottles were then stoppered and set aside for about eighteen hours, or over night, by which time a clear solution was obtained if the acid used was over 90 per cent H_2SO_4, but if of less strength a residue, presumably of potassium sulphate, was left. The contents of the weighing-bottles were transferred to the decomposing bulb with the aid of a wash-bottle containing acid of the same strength as that used in the weighing-bottles. In each determination 32 c.c. of acid were used. The strengths of sulphuric acid used and the volume in cubic centimetres of nitric oxide (NO) per grm. of potassium nitrate for each acid are as follows:—

Strength of sulphuric acid in per cent.	C.c. of nitric oxide per grm. potassium nitrate. I.	II.	III.	IV.	V.	Average.
98·03	222·0	221·8	222·0	222·3	222·3	222·08
96·92	223·2	223·0	223·3	223·3	—	223·2
96·92	224·0	224·3	224·4	224·4	224·4	224·3
95·14	225·1	224·8	225·0	225·2	225·0	225·0
94·07	225·0	225·0	224·9	225·2	225·0	225·02
93·05	225·1	225·0	224·8	224·9	225·0	224·96
90·90	225·0	224·9	224·9	225·0	225·0	224·96
85·04	225·3	225·1	225·3	225·0	225·3	225·2
80·14	226·2	226·0	226·2	226·2	226·0	226·1

A difference of 4·02 c.c. of nitric oxide is thus obtained by the use of the strongest and weakest acids. It seems probable that this is due to the varying absorptive powers for nitric oxide, of the different strengths of sulphuric acid used.

Lunge (*Journ. Soc. Chem. Ind.*, 1885, p. 447) states that "1 c.c. of concentrated vitriol dissolves 0·000593 grm. = 0·035 c.c. NO." If this 4·02 c.c. of nitric oxide per grm., or 2·01 per half grm. of potassium nitrate, is due to the difference of solubility of nitric oxide in the first and last acids used, then 32 c.c. of 98·03 per cent sulphuric acid absorbs 2·01 c.c. nitric oxide, and 1 c.c. absorbs 0·0628 c.c. nitric oxide. For nitrometer work acid of about 95 per cent H_2SO_4 appears to be the best. Weaker acid attacks the mercury more readily, and decomposes nitric acid more slowly. There is no objection to stronger acid except the difficulty of obtaining it. The chemically pure acid made by a well-known company has been found to vary from 95·0 to 98·0 per cent H_2SO_4.—*Journal American Chemical Society*, xxiii., No. 4.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 4, July 22, 1901.

Experiments with Uranium at Very Low Temperatures.—Henri Becquerel.—The author examines the action of liquid air on uranium, with regard to its radio-activity. The action is measured by means of an extremely delicate electroscope. At the temperature of boiling air the current apparently is reduced to one-half of that obtained by the action of the uranium at a temperature of 24·8°. The author also repeats the experiment already performed by Prof. Dewar of plunging into liquid air, or better into liquid hydrogen, a crystal of uranium nitrate, the latter becoming spontaneously luminous.

The Nature of X Rays.—Jules Semenov.—The author's experiments lead him to the conclusion that X rays represent the directions of transmission, through the medium of ether, of electric vibrations. These vibrations are communicated to all bodies which they meet during their passage. When the bodies are charged with electricity, and when they are protected against discharge by convection, they lose their charge by radiation.

Action of Hypophosphorous Acid on Acetone.—C. Marie.—Crystalline hypophosphorous acid appears to have no action when heated with acetone. However, if the solution is kept boiling for some time the temperature rises

regularly, the liquid at the same time becoming more and more brown coloured and viscous. On cooling, crystals separate out. These have the formula—

$$C_6H_{15}O_4P = 2PO_2H_3 + 2C_3H_6O,$$

and are a monobasic acid. A second body can be obtained from the filtrate. This latter is a bibasic acid characterised by the insolubility of its lead salt. It has the formula $C_3H_9O_4P = PO_3H_3 + C_3H_6O$.

Preparation of Pure Cerium Oxide.—Jean Sterba.—The author modifies MM. Wyrouboff and Verneuil's method of preparation of pure cerium. He uses electrolysis as an agent of oxidation, this rendering the operations much more rapid. Cerium oxide when perfectly pure can have a decided colour, but when prepared with elimination of nitrogen it becomes snow white. The action of hydrogen on cerium oxide effects an incomplete reduction and formation of Ce_2O_3. Zinc also reduces the oxide CeO_2.

Thermic Examination of the Hydrates of Solid Soda.—M. de Forcrand.—M. Berthelot gives for the heat of solution of NaOH the number +9·78 cals. at 10·5°, whilst for a specimen of pure commercial soda of composition $NaOH + 0.76H_2O$ the number +7·31 cals. is given. Thomsen gives +9·94 cals. as the heat of solution of NaOH at 17·32°. The author re-examines these numbers and uses them to discover a number of solid hydrates:—$3NaOH + 2H_2O$, $NaOH + H_2O$, $2NaOH + 7H_2O$.

Oxidation of Propylglycol by Mycoderma aceti.—André Kling.—The bacteria of sorbose and the *Mycoderma aceti* of Orleans act in the same manner on racemic propylglycol, oxidising the secondary alcoholic function of the left isomer and transforming it into acetol. The author intends to complete this investigation of the parallelism of the action of the two ferments and to extend it to other glycols.

Action of Pyridic Bases on Tetrahalogen Benzoquinones.—Henri Imbert.—The author previously announced that pyridic bases act on chloranile and bromanile, giving substitution bodies of phenolic function, if, however, one of the α-positions of the pyridic radicle is not taken. The pyridine and the tetrachloroquinone, for example, give the derivatives $C_5H_4N-C_6Cl_2O_2-OH$ or $HO-C_5H_2N=C_6Cl_2O_2$. These bodies easily lose an atom of chlorine under the influence of alkalis.

The Hydrobromic and Hydrochloric Ethers of the Supposed Bi-naphthylene-glycol.—R. Fosse.—Under the name of aromatic glycol Rousseau described a derivative of binaphthylene which should possess the formula—

$$\begin{array}{l} C_{10}H_6-C-OH \\ \quad\quad\quad\

THE CHEMICAL NEWS

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ON THE BEHAVIOUR OF OXY-HÆMOGLOBIN, CARBONIC-OXIDE-HÆMOGLOBIN, METHÆMOGLOBIN, AND CERTAIN OF THEIR DERIVATIVES, IN THE MAGNETIC FIELD, WITH A PRELIMINARY NOTE ON THE ELECTROLYSIS OF THE HÆMOGLOBIN COMPOUNDS.*

By ARTHUR GAMGEE, M.D., F.R.S.,
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1. *The Observations of Faraday and Plücker on the Diamagnetic Properties of the Blood.*

In the course of his investigations on magnetism and diamagnetism, read before the Royal Society in the year 1845, Faraday ("On New Magnetic Actions and on the Magnetic Condition of all Matter," *Phil. Trans.*, 1846, Part I.), found that, notwithstanding the iron which its colouring matter contains, the blood is a diamagnetic liquid. "I was much impressed," he remarked, "by the fact that blood was not magnetic, nor any of the specimens tried of red muscular fibre of beef or mutton. This was the more striking, because, as will be seen hereafter, iron is *always* and in almost all states magnetic. But in respect to this point it may be observed that the ordinary magnetic property of matter and this new property are in their efforts opposed to each other; and that when this property is strong it may overcome a very slight degree of ordinary magnetic force, just as also a certain amount of magnetic property may oppose and effectually hide the presence of this force" (Faraday's "Experimental Researches in Electricity," 1855, vol. iii., p. 36, para. 285). Faraday further found the blood to behave like all the constituent tissues of animal bodies which he investigated, and was led to state that "if a man could be suspended with sufficient delicacy, after the manner of Dufay, and placed in the magnetic field, he would point equatorially; for all the substances of which he is formed, including the blood, possess this property" (Faraday's "Experimental Researches in Electricity," vol. iii., p. 36, 2281).

De la Rive and Brunner,† later, suspending a bound-up frog between the poles of an electro-magnet, observed it to assume an equatorial position, thus realising Faraday's prediction that a complex animal organism must be diamagnetic in accordance with the properties of its constituent tissues and of the water which enters so largely into their composition.

Shortly after the publication of Faraday's researches on diamagnetism, Professor Plücker,‡ of Bonn, in a well known paper, which appeared in 1848, after describing the characteristic behaviour of magnetic and diamagnetic liquids contained in watch-glasses placed upon and between the poles of powerful electro-magnetics, gave the results of his observations on the diamagnetic properties of the blood. He not only confirmed, by experimenting on the blood of the frog, of man, and of the ox, the accuracy of Faraday's statements, but by employing the microscope in his observations he was able to show that the blood corpuscles are more strongly diamagnetic than the liquid in which they float.*

2. *Objects of the present Investigation.*

At a time when all facts bearing on the physical properties and the chemical relations and structure of the blood-colouring matter are rightly claiming the attention of many of the leading workers in physiological chemistry, it appeared to me very desirable to examine the magnetic properties of the crystalline blood-colouring matter itself, in the condition of utmost available purity, and, whatever the results might be to extend the inquiry to its leading iron-containing derivatives.

Although Faraday had shown that the blood is diamagnetic, and Plücker that the blood corpuscles are more decidedly diamagnetic than the liquid in which they float, it was yet conceivable, though improbable, that the iron-containing hæmoglobin would prove to be a feebly magnetic body, of which the true magnetic behaviour was concealed by the substances with which it is associated in the blood corpuscles. Whether hæmoglobin proved to be magnetic or diamagnetic, it obviously would be of great interest to examine the magnetic properties of the iron-containing substances which the blood-colouring matter yields when it is decomposed by acids in the presence of oxygen, and in the event of a difference between the magnetic behaviour of the mother-substance and its derivatives, to push the inquiry in a direction likely to lead to the discovery of the cause of the discrepancy. In pursuance of such an object I have been led to inquire whether the pure blood-colouring matter in aqueous solution is an electrolyte, and having discovered that it is one, to examine the results of its electrolysis. On this part of my inquiry the statements which I have to make in this paper are strictly preliminary, and, except in the first most interesting particular that oxy-hæmoglobin and CO-hæmoglobin separate in the first instance from their aqueous solutions when these are subjected to very feeble currents, are to be considered as liable to correction by future more extended work.

3. *The Electro-magnet employed in the present Research.*

The electro magnet employed was constructed by Ladd many years ago, and is sufficiently powerful to be employed for observations on the rotation of the plane of polarisation of light. I had it fitted with an accurately closing glass case, and with adequate arrangements for the proper suspension of the bodies under examination. I am not possessed of instruments which would enable me to determine directly the strength of the magnetic field employed in my several sets of experiments. The Rev. F. J. Jervis-Smith, F.R.S., Millard Lecturer in Experimental Mechanics in the University of Oxford, to whom I had the pleasure of showing my experiments, had the great kindness to make careful measurements of the coils, and has practically re-constructed an electro-magnet similar in dimensions to mine, with the same windings, and of which the iron core derived from a similar instrument made by Ladd, was probably identical in properties to that in my electro-magnet. Using Professor Rowland's method for determining the field, he obtained the following results:—

Intensity of the earth's horizontal magnetic component at Oxford = 0·18.

Distance between faces of pole pieces, 3 c.m.

* A Paper read before the Royal Society, June 20, 1901.

† De la Rive and Brunner's researches are only known to me at second-hand from the account given of them in Valentin's "Grundriss der Physiologie" (4 Auflage, 1855, p. 507), where an engraving is reproduced in which a bound-up frog is shown placed between the poles of the electro-magnet.

‡ Plücker, "Experimental Untersuchungen über die Wirkung der Magnete auf gasformige und tropfbare Flussigkeiten." Refer to the heading "Über das magnetische und diamagnetische Verhalten der tropfbarflussigen Körper," in *Poggendorff's Annalen der Physik und Chemie*, 1848, vol. lxxiii., para. 49, p. 575.

* In 1874, Dr. R. C. Shettle, in a paper read before the Royal Society (*Roy. Soc. Proc.*, 1875, vol. xxiii., pp. 116—120), gave the results of experiments which had led him to the conclusion that arterial blood is paramagnetic as compared with venous blood, which is diamagnetic, the assumed difference in magnetic behaviour being explained by the author as to the paramagnetic properties of the oxygen absorbed by venous blood. In reference to these statements the only observation which I have to make, on the basis of my own work, is that they are entirely erroneous.

Current in ampères.	Magnetic field in C.G.S. units.
2·4	516
3·3	700
4·2	870

Probably it is safe as an approximate estimate to assume that my field was about 1000 C.G.S. units with a current of 5 ampères.

All the fundamental experiments on the magnetic properties of oxy-hæmoglobin, CO-hæmoglobin, and methæmoglobin were made by suspending cakes of the dried crystalline bodies by means of one or a few fibres of silk between the poles, thus avoiding the disturbing influence of glass tubes, however feebly magnetic. In the case of hæmin the substance was similarly examined, in the first instance, by suspending as far as possible rectangular cakes formed by the aggregation of crystals. In the case of hæmatin, the substance being in an amorphous pulverulent condition, was necessarily examined in glass tubes, but its intensely magnetic properties prevented in its case, as in that of hæmin, any difficulties arising from the very feebly magnetic properties of the glass tube containing it.

4. Oxy-hæmoglobin a strongly Diamagnetic Body.

The oxy-hæmoglobin employed in the present research was prepared by myself during the past winter from the blood of the horse by employing substantially the method of Hoppe-Seyler. In some cases the blood corpuscles were separated from the defibrinated blood by long continued centrifugalising; generally, however, the defibrinated blood was mixed with ten times its volume of a mixture made by diluting 10 volumes of saturated NaCl solution with 90 volumes of distilled water, and the corpuscles were then separated by means of the centrifuge.

In either case, the magma of corpuscles were treated with a small quantity of distilled water and pure ether, and the mixture having been thoroughly agitated in a stoppered separating funnel, the aqueous solution of the blood-colouring matter was separated, and filtered into flasks surrounded with ice, and subsequently treated with one-fourth of its volume of pure absolute alcohol at a temperature of −5° C., and the mixture placed in an ice chamber for twenty-four or thirty-six hours. The oxy-hæmoglobin which crystallised was separated from its mother-liquor by means of the centrifuge. The crystalline mass was repeatedly washed with distilled water at 0° C., and the washed crystals treated with distilled water at 30° C.; the saturated solution was rapidly centrifugalised, rapidly filtered into flasks surrounded by ice and salt, and the hæmoglobin caused to crystallise by the addition of absolute alcohol under the prolonged influence of cold. After being crystallised three times, the oxy-hæmoglobin was collected on filters, and the moist mass of microscopic crystals drained. The pasty crystalline mass was dried *in vacuo* over sulphuric acid at a temperature which never exceeded 5° C.

Behaviour in the Magnetic Field.—An irregular mass of three times crystallised oxy-hæmoglobin dried *in vacuo*, weighing 1·088 grms., and measuring 18 m.m. in length, 13 m.m. in depth, and 13 m.m. in breadth, was suspended by a couple of fibres of unspun silk between the poles of the magnet, the distance between these being 20 m.m.; the mass was made to rest in the axial position before the current was passed through the coils.

Three cells of an accumulator were employed; on closing the key the mass of hæmoglobin instantly assumed the equatorial position. The experiment was repeated with masses of hæmoglobin prepared at various times, and re-crystallised from one to three times, and weighing from 0·5 to 2 grms., and invariably they were found to be powerfully diamagnetic.

A specimen of oxy-hæmoglobin of the horse, kindly prepared for me under the direction of Professor Hofmeister in the Chemico-Physiological Laboratory of the University of Strasburg, by the ammonium-sulphate method, and which had been five times crystallised, proved to be as powerfully diamagnetic as the oxy-hæmoglobin prepared by Hoppe-Seyler's method.

5. Carbonic-oxide-hæmoglobin is, like Oxy-hæmoglobin, strongly Diamagnetic.

Mode of Preparation.—The carbonic oxy-hæmoglobin employed was prepared by saturating a concentrated solution of twice crystallised oxy-hæmoglobin with pure CO, and then crystallising the CO compound by the addition of absolute alcohol and exposure to a temperature of −5 to 10° C.

Behaviour in the Magnetic Field.—A nearly rectangular prismatic mass of CO-hæmoglobin which had been dried *in vacuo*, and which weighed 0·642 grm., and of which the length was 17 m.m., the breadth 6·5 m.m., and the depth 13 m.m., was brought into the axial position between the poles of the electro-magnet, the distance between these being 18 m.m. On passing the current from three cells of an accumulator through the coils of the electro-magnet the mass instantly assumed the equatorial position. The experiment was repeated with different specimens of CO-hæmoglobin, and invariably with the same result.

In the absence of all data as to the diamagnetic moment of either oxy- or CO-hæmoglobin, it is impossible to state whether these bodies differ in any degree in respect to their behaviour in the magnetic field. Working carefully but merely qualitatively, it would appear, however, that their behaviour in the magnetic field is identical.

6. Methæmoglobin is, like Oxy-hæmoglobin, strongly Diamagnetic.

The substance was prepared by adding to a saturated solution of twice crystallised oxy-hæmoglobin of the horse a few drops of solution of ferricyanide of potassium until the characteristic change in colour and in the spectrum indicated the complete conversion into methæmoglobin. The solution was cooled to −5° C., treated with one-fourth of its volume of absolute alcohol at −10° C., and the mixture placed in ice and salt for a period of thirty-six hours. The crystalline methæmoglobin which separated was then washed with repeated quantities of ice-cold water, collected on a filter, drained, and dried *in vacuo* at a temperature not exceeding 5° C. Experiments with lumps of this substance varying in weight between 0·3 and 1·0 grm. showed it to be apparently as diamagnetic as oxy-hæmoglobin.

6. Hæmatin and Acethæmin (Hæmin)—Intensely Magnetic Substances. Preliminary Remarks.

The more recent analysis of Jaquet, Zinoffsky, and Hüfner have led to the conclusion that, at any rate in the horse, the dog, the ox, and the hen there exists a remarkable constancy in the proportion of the iron which exists in hæmoglobin (0·335 per cent).* If it be assumed that 1 molecule of hæmoglobin contains 1 atom of iron, the molecular weight of the hæmoglobin of the dog, the horse, the ox, and the hen would be 16,669, a result which concords admirably with the volume of oxygen and carbonic oxide which can enter into combination with hæmoglobin on the assumption (first of all advanced by Lothar Meyer) that 1 molecule of hæmoglobin can combine either with a molecule of oxygen or of carbonic oxide. The empirical formula for the hæmoglobin of the dog calculated by Jaquet from his analysis is probably very near the truth, namely, $C_{75}H_{1203}N_{195}S_3FeO_{218}$.

Why should hæmoglobin possess so enormously high a molecular weight? The question suggested itself to Bunge, who has furnished us with a reason which is eminently suggestive:—"The enormous size of the hæmo-

* For a discussion of all the more recent analyses of hæmoglobin, see my article on "Hæmoglobin" in Shäfer's "Text-book Physiology," p. 199, *et seq.*

globin molecule," says this writer, "finds a teleological explanation, if we consider that iron is eight times as heavy as water. A compound of iron, which would float easily along with the blood current through the vessels, could only be secured by the iron being taken up by so large an organic molecule."

When oxy-hæmoglobin is subjected to the action of acids and alkalis it splits up with great ease into a coloured iron-containing body, and into an albuminous body (or mixture of such bodies). The former, to which the name of Hæmatin has been given, is a derivative of the molecular group existing in the blood-colouring matter, upon which its colour, its spectroscopic characters, and its physiological properties doubtless depend, *though it is a derivative which is unquestionably a product of oxidation, and in no sense represents the real hæmochromogen.* According to Hoppe-Seyler, the empirical formula of hæmatin is $C_{34}H_{35}O_5N_4Fe$, whilst according to Nencki its composition is represented by the formula $C_{32}H_{32}O_4N_4Fe$.

When the decomposition of oxy-hæmoglobin is effected by glacial acetic in the presence of alkaline chlorides, a perfectly crystalline substance separates, which has been hitherto known under the name of *hæmin*, but which we shall now, following the suggestion of Nencki, term *acethæmin*. This body was looked upon by Hoppe-Seyler as a hydrochloride of hæmatin; the recent researches of Nencki and Zaleski have shown that acethæmin contains 8·59 of iron, and possesses a composition represented by the formula $C_{34}H_{33}O_4N_4ClFe$; it contains an acetyl group, and both the acetyl and chlorine in it are linked to the iron. When this body is dissolved in weak solutions of sodium hydrate in the cold, the chlorine and acetyl are separated, and on neutralisation with acids, hæmatin of composition $C_{32}H_{32}O_4N_4Fe$ is obtained. It is with these two coloured iron-containing decomposition products of hæmoglobin, hæmatin, and acethæmin that my observations have been carried out. Before referring to these in detail, I wish again to insist that these oxidation-products in no sense represent the unaltered iron-containing group to which the blood-colouring matter owes its physiological properties. As Hoppe-Seyler showed, when hæmoglobin is decomposed by acids and alkalis *in the absence of all traces of oxygen*, hæmatin is never formed, but a colouring matter which possesses the same spectrum as that which had previously been described by Stokes as that of reduced hæmatin.

This substance Hoppe-Seyler called hæmochromogen, and he expressed the opinion that it constitutes the veritable colour radical upon which the physiological properties of hæmoglobin depend. The experimental facts advanced by Hoppe-Seyler have always appeared to me absolutely inadequate to warrant this hypothesis, which, however, is most suggestive, and demands a thorough and a new investigation.

A. *Magnetic Properties of Acethæmin.*

The acethæmin employed in the present research was prepared by me from ox's blood by the method of Schalfijew. Some of the specimens were purified by re-crystallisation from glacial acetic acid, others by dissolving in a chloroformic solution of pure quinine, and subsequently adding to the filtrate hot glacial acetic acid, saturated with NaCl.*

My first observations were made with a block of agglomerated hæmin crystals weighing 0·6455 grm., and measuring 26 m.m. in greatest length, 18 m.m. in height, and 6 m.m. in thickness; this block was suspended by two fibres of silk, so as to occupy the equatorial position in reference to the pole pieces of the magnet. The distance between the poles being 30 m.m., on passing a current from three accumulator cells through the coils, the mass instantly assumed the axial position, and was strongly attracted to the nearest pole, the suspending silk fibres being sensibly deflected from their original vertical position. Even when the poles of the electro-magnet were 40 m.m. apart, the mass instantly set in an axial position when the current was passed. The observations were repeated with numerous specimens of hæmin, and always with similar results.

B. *Magnetic Properties of Hæmatin.*

The hæmatin employed in these researches was prepared by dissolving re-crystallised and perfectly pure acethæmin in a weak solution of chemically pure sodium hydrate at ordinary temperatures, and precipitating the filtered solution without delay by neutralising with dilute sulphuric acid. The precipitated hæmatin was thoroughly washed, drained, and dried. In consequence of its absolutely amorphous pulverulent character, my magnetic observations on this body were conducted with the aid of tubes of very feebly magnetic glass, containing from 0·1 to 0·4 of pure hæmatin. The intensely magnetic character of hæmatin was as easily demonstrated as had been that of acethæmin.

7. *Preliminary Observations on the Electrolysis of Solutions of Pure Oxy-hæmoglobin and* CO-*hæmoglobin.*

The remarkably definite results of my research, which had shown that oxy- and CO-hæmoglobin are decidedly diamagnetic substances, whilst their iron-containing derivatives, acethæmin and hæmatin, are powerfully magnetic, naturally led me to speculate on the possible cause of these differences. It appeared to me that if hæmoglobin were found to be an electrolyte, apart from the interest which would attach to the discovery of the fact, a study of the products of its electrolysis might throw great light upon the question. Do we not know, for instance, that those compounds in which iron and other magnetic metals are present in electro-negative radicals are diamagnetic?*

In spite of my having made great efforts to purify as completely as possible the substances with which I worked, it is questionable whether their purity was sufficient for electrolytic researches. The experiments which I have yet made on this division of my subject must therefore be looked upon as strictly preliminary, and I hope in the course of the coming winter to extend them greatly, making use of compounds of hæmoglobin which have been subjected to far more frequent re-crystallisation. In the course of these experiments, beside studying the proximate products of electrolysis with currents of different strength and potential, I intend to determine by the methods of Kolhrausch and Ostwald, with as great accuracy as possible, the specific conductivities of solutions of oxy- and CO-hæmoglobin.

The following are the results of my electrolytic experiments which I wish at present to place on record:—

Firstly. When solutions of pure oxy-hæmoglobin are subjected to electrolysis at a temperature of about 15° C. between platinum electrodes, from twelve to sixteen cells of a carbon zinc bichromate battery being employed, and the current passing through the liquid being from 3 to 5 milliampères, a rapid subsidence of the colouring matter takes place, the upper layers of the solution becoming perfectly colourless. The depositing colouring matter retains the spectroscopic character of oxy-hæmoglobin, and when stirred with it is absolutely and almost instantaneously soluble in the liquid from which it has separated. Exactly the same result occurs in the case of carbonic-oxide-hæmoglobin.

Secondly. On continuing the passage of the current through the solution in which precipitation has occurred,

* Refer to my previously quoted article in Schäfer's "Text-book of Physiology," and to Nencki and Zaleski's recent article, 'Untersuchungen uber den Blutfarbstoff. I. Ueber die Aether des Hämins," *Zeitschrift fur Physiologische Chemie*, 1900, vol. xxx., p. 384, *et seq.*

* Miller, "The Elements of Chemistry," Part I., "Chemical Physics," p. 422, London, 1855; H. du Bois, "Propriétés magnétiques de la matière pondérable, Rapports présentés au Congrès Internationale de Physique réunis à Paris en 1900," Paris, 1901, Tome II., p. 460.

secondary reactions occur, gas is developed both at the anode and cathode, and in many cases a dirty white-brown deposit forms at the cathode.

Thirdly. Under conditions of strength of current and potential which were not determined with sufficient accuracy, and which I have not yet been able to reproduce at will, the solutions of oxy-hæmoglobin and CO-hæmoglobin have, under the long continued action of the current, on several occasions deposited at the anode an insoluble red colouring matter containing both the albuminous and the iron-containing residues of hæmoglobin. In the case of CO-hæmoglobin the compound deposited has presented the peculiar colour of CO-hæmoglobin.

8. *General Conclusions.*

The following are the conclusions to which I have been led by my experiments.

1. The blood-colouring matter, oxy-hæmoglobin, as well as carbonic-oxide hæmoglobin, and methæmoglobin, are decidedly diamagnetic bodies.

2. The iron-containing derivatives hæmatin and acethæmin are powerfully magnetic bodies. The differences in magnetic behaviour between the blood-colouring matter and acethæmin and hæmatin point to the profound transformation which occurs in the hæmoglobin molecule when it is decomposed in the presence of oxygen.

3. The preliminary study of the electrolysis of oxy-hæmoglobin and CO-hæmoglobin renders it probable that, in the blood-colouring matter, the iron containing group, on which its physiological properties depend, is (or is contained in) an electro-negative radical; according to analogy, the iron in such a compound would possess diamagnetic and not magnetic properties.

In conclusion, I beg to acknowledge my indebtedness to Professor von Bunge, of Basel, to Professor Franz Hofmeister, of Strassburg, and to Dr. v. Ehrenberg, the technical director of the chemical factory of Messrs. Merck, of Darmstadt, for their great courtesy and kindness in placing at my disposal preparations of hæmoglobin prepared by themselves or under their direction.

RADIO-ACTIVITY OF RADIUM SALTS.

By P. CURIE and A. DEBIERNE.

We have already shown that it is possible to communicate radio-active properties temporarily to any body by means of radium salts, and in particular such properties can be given to distilled water.

Water can be rendered radio-active by several methods. It is possible, for example, as we have already shown, to separate by distillation in an absolutely air-tight vessel the water from a solution of radium chloride several days old. The distilled water thus obtained is strongly radio-active.

A second method, still simpler, consists in placing two crystallising vessels into a closed space, one containing a solution of a radium salt, and the other distilled water. After a time the distilled water becomes radio-active, the radio-activity having been communicated by the gas in the closed vessel.

Finally, a third method consists in enclosing a solution of radium salt in a hermetically sealed celluloid capsule, and plunging this capsule into another closed vessel of distilled water. Under these conditions the celluloid plays the part of a perfectly semi-permeable membrane, and no trace of salt passes through the walls, whilst the activity of the solution is to a great extent communicated to the external water. This induced activity cannot be transmitted by the air across a wall of dry celluloid, but is easily transmitted if the wall is wetted with a drop of water.

Water can be made very strongly active, and, under certain conditions, even more so than that of the body under the influence of which it is rendered radio-active. When kept in a sealed tube, however, the water loses the greater part of its activity in a few days.

When in an open vessel the loss of activity is much more rapid, and is more rapid according as the surface of contact with the air is increased.

Solutions of radium salts behave in an analogous manner. If a solution is left in an open vessel, the activity is considerably diminished, the diminution being more rapid the greater the area of solution in contact with air. But such a solution differs from radio-active water in that the loss of activity is not absolute, for if the solution, after losing its activity, is placed in a sealed tube, it gradually acquires in the course of ten days or so its original activity.

From these observations we are able to deduce a theory which explains various phenomena of radio-activity. It is necessary to admit that each atom of radium acts as a continual and constant source of radio-active energy without knowing precisely where this energy goes.

The radio-active energy accumulated in a body from a mass of radium tends to dissipate itself in two different ways:—(1). By radiation (rays charged and not charged with electricity), (2) by conduction to a body in contact or transmission from particle to particle through the medium of gases and liquids (induced radio-activity). The loss of radio-active energy of a body, as much by radiation as by conduction, is far greater as the quantity of this energy accumulated in the body increases.

It must be understood that an equilibrium is necessarily established. Radio-active energy accumulated in the body goes on increasing until the double loss of which we shall speak later compensates the continual increase of energy furnished by the radium.

We must consider this point of view as analogous to that which is used during an investigation of calorific phenomena. If, in the interior of a body, a continued and constant evolution of heat takes place, the heat accumulates in the body, and the temperature rises until the loss of heat of the body by radiation and conduction make an equilibrium. By following this analogy we must consider a radio-active tension as analogous to temperature and characterised by intensity of radiation (which up to this point we have considered as giving a measure of the intensity of radio-activity). We can thus define a capacity of radio-activity in an analogous manner to calorific capacity.

The theory which we have just put forward can be made to explain various phenomena. In general, except under special conditions, the activity is not communicated from particle to particle across solid bodies. When a solution is preserved in a sealed tube the loss by radiation only consists in this, and the radio-activity of the solution takes a very high value. If, on the contrary, the solution is placed in an open vessel, the loss of activity from particle to particle by conduction becomes considerable, and when a state of equilibrium is established the radio-activity of the solution is very feeble.

We must also remark that the activity of a solid radio-active body left free to the air does not diminish sensibly, because the propagation of the radio-activity by conduction does not take place across solids, it being only an extremely thin superficial layer which is capable of producing the induced radio-activity. We have proved that a solution of the same salt produces much more intense phenomena of induced radio-activity (twenty times greater) than the salt itself. With a solid salt the radio-active energy accumulates in the salt and is scarcely dissipated at all by radiation. On the contrary, when the salt has been in solution for several days, the radio-active energy is divided between the water and the salt, and if the salt and water are separated by distillation the water contains a great part of the activity, and the solid salt is much less active (ten or fifteen times, for example), than before solu-

tion. When left to itself the solid salt regains little by little its original activity.

The communication of the activity of a radium salt to its water of solution is, however, very slow, and the equilibrium is only obtained at the end of about ten days; if, for example, we evaporate such a solution shortly after it is made, the salt retains a much more considerable portion of its radio-activity.—*Comptes Rendus*, vol. cxxxiii., No. 5, July 29, 1901.

THE ASSAYING OF COMPLEX GOLD ORES.*

By ERNEST A. SMITH, Assoc.R.S.M., F.C.S., late Assistant Instructor in Assaying, Royal School of Mines, London.

(Continued from p. 75).

Antimonial Ores.—Owing to the very fusible and volatile nature of antimony sulphide, and also of the oxide its decomposition gives rise to, it is usual to avoid the roasting of antimonial ores by employing nitre to effect the oxidisation. The chief drawback to the use of nitre is the difficulty of regulating the quantity to be employed, which can only be learnt by experience. The adjustment of the quantity of nitre is simplified when one sulphide only is present, but this is a condition of things seldom met with in practice. Many text-books give elaborate formulæ for arriving at the quantity of nitre needed for any particular class of ore, but the best of these frequently fail to give reliable results. A formula may sometimes serve as a rough guide, but practical experience alone will enable the assayer to adjust the proportion of nitre.

The quantity may be approximately determined by fusing 5 grms. of the ore with 100 grms. of litharge and 10 grms. of sodium carbonate. The lead resulting from the fusion is weighed, and from this weight is calculated the quantity of lead which would be obtained from the quantity of ore to be used for assay (usually 50 grms.). Deduct 30 (the weight of lead required to collect the gold) from this result, and divide by 5; the figure obtained gives approximately the quantity of nitre necessary to be added.

The difficulty of adjusting the quantity of nitre is largely dependent on the following fact, that sulphur, and in some cases the metals, are capable of two degrees of oxidation, and whether the lower or the higher oxide is formed by the action of the nitre will depend very largely on the conditions of the fusion. In this connection the character of the slag produced is an important factor. When the slag is acid owing to the presence of much siliceous material in the charge, the sulphur will, in most cases, be eliminated as sulphurous oxide (SO_2), and the lower oxide of the metal be formed. On the other hand, if the slag contains much soda, the tendency will be for the sulphur to be oxidised to sulphate (sulphuric acid, SO_3), and the metal converted to the higher oxide.

Sodium carbonate is the most suitable flux for antimonial ores, as it forms readily fusible compounds with the antimony oxides resulting from the action of the nitre. The quantity of sodium carbonate required for ores consisting mainly of stibnite is about equal to the weight of the ore taken.

When sulphides of other metals are present, borax may be substituted for a part of the sodium carbonate, as it is the best flux for the metallic oxides formed during the process.

Nitre may be employed according to either of the following methods:—

I. To effect partial oxidation.
II. To effect complete oxidation.

In the former case, the quantity of nitre added is sufficient to oxidise a portion only of the oxidisable substances, the remaining portion being oxidised by the lead oxide with the production of metallic lead, which sinks through the molten mass and collects the gold and silver.

In the second method, usually known as Balling's method, sufficient nitre is added to effect the complete oxidation of the oxidisable substances, a mixture of litharge and charcoal being subsequently added to supply lead for collecting the gold and silver.

Method I. Partial Oxidation.—The following proportions are suitable for an antimonial ore containing about 75 per cent of stibnite, and will act as a guide for the quantity of nitre needed for this class of ores:—

Ore	50 grms.
Red-lead	100 ,,
Sodium carbonate ..	40 ,,
Borax	10 ,,
Nitre	30 to 40 ,,

With cover of powdered salt.

The fusion of charges containing nitre is effected in large crucibles at a comparatively low temperature, care being taken to avoid a sudden increase of temperature, as fusion takes place somewhat quickly and the slags are in most cases very fluid. When effervescence has ceased, and the contents of the crucible have become thoroughly liquid and tranquil, it is advisable to lift the crucible out of the fire, and subject it to a rotary motion in order to thoroughly mix the liquid contents. If this treatment causes effervescence it indicates that the action of the nitre is not complete, and the crucible must be returned to the fire, and the fusion continued.

The button of lead obtained should weigh between 25 and 35 grms., but if below or above this weight, the charge must be modified to produce the required weight.

Experience has shown that, as a general rule, from 0·25 to 0·30 part of nitre are required to oxidise the quantity pyritic material which would act as a reducing agent to produce one part of lead, or, in other words, the addition of 1 grm. of nitre will decrease the weight of the lead button by from 4 to 5 grms. Conversely, the weight of the lead button may be increased by from 4 to 5 grms. by diminishing the quantity of nitre by 1 grm. The weight of lead obtained will vary somewhat according to the quantity and nature of the fluxes used and the conditions of the fusion.

Until experience has been gained, the first assay of an ore of unknown composition may be more or less unsatisfactory, but the result obtained from the fusion will indicate what modification of the charge is necessary to give a satisfactory result.

When insufficient nitre is used the lead button is brittle, and resembles galena owing to the presence of sulphur; it is also frequently accompanied by a layer of regulus.

With due attention, the nitre may be so adjusted that a malleable button, comparatively free from antimony, will be obtained, and may be cupelled direct. If the button is brittle, comparatively hard, and white, it generally contains antimony, in which case it must be scorified with the addition of more lead if necessary before being cupelled.

The slags from comparatively rich ores should be cleaned in the manner already described under basic ores.

Method II. Complete Oxidation (Balling's Method).—By this method a quantity of nitre equal to twice the weight of the pyritic material in the ore is usually sufficient to effect complete oxidation, but in exceptional cases rather more than this amount may be required. Borax and sodium carbonate are added as in the previous method to flux the metallic oxides formed, but the red-lead is omitted. The fusion is conducted as before, and when the action of the nitre is complete, and the contents of the crucible are in tranquil fusion, it is withdrawn from the fire and allowed to cool until the slag begins to thicken. A mixture of 40 grms. of red-lead, 2 grms. of charcoal powder, and 10 grms. of borax is then added, the crucible returned to the furnace, and the charge kept in a molten condition for from ten to fifteen minutes. When

* Abstract of Paper read before Institution of Mining and Metallurgy, May 15, 1901.

all action has ceased, the contents of the crucible are poured into a mould in the ordinary way. By this means the globules of metallic lead obtained by the reduction of the red-lead sink through the molten slag, and collect the gold and silver.

Baling's method of complete oxidation requires a little more time than the method of partial oxidation, but the lead button obtained by the former method is always of the required weight, and is usually comparatively free from antimony, and may generally be cupelled direct. Both methods, however, give equally satisfactory results when due precautions are taken.

Antimonial ores sufficiently rich in gold to allow of comparatively small quantities being used for assay may be oxidised by means of lead oxide instead of nitre. In this case the stibnite is oxidised by the lead oxide with the production of antimony oxide and metallic lead, which latter acts as a collecting agent for the gold and silver ($Sb_2S_3+9PbO=Sb_2O_3+3SO_2+9Pb$.) Stibnite requires from fifteen to twenty times its weight of lead oxide to effect oxidation.

Combined Wet and Dry Method.—The following method, involving solution of the ore, may be conveniently employed for antimonial ores as a check upon other methods. It possesses the advantage of producing lead buttons practically free from antimony, and thus avoiding the necessity of scorification previous to cupellation. The weighed quantity of ore (from 30 to 50 grms.) is treated with concentrated hydrochloric acid, and heated until decomposition is complete; the solution is diluted with a small quantity of water in which a few crystals of tartaric acid have been dissolved. The insoluble residue is allowed to settle, and when the solution is clear as much of the liquid as possible is poured off through a filter without disturbing the residue. The residue is finally transferred to the filter, allowed to drain, and then dried. The filter-paper is burnt, and the ash, with the insoluble residue, is scorified with ten times its weight of granulated lead and a cover of borax, or it is fused with the following fluxes:—

Red-lead	30 grms.
Charcoal powder	1·5 „
Sodium carbonate and borax, varying together up to ..	30 „

The fusion is effected in the ordinary way, and the resulting lead button cupelled direct.

(To be continued).

CONTRIBUTIONS TO THE SCIENCE OF THE NITROCELLULOSES.*

By G. LUNGE and J. BEBIE.

(Continued from p. 77).

Partial nitration ensues on using nitric acid 1·4 alone, even without addition of sulphuric acid. In this case very little oxycellulose is formed (0·0018 grm. methyl-blue per 1 grm.). Hence the cellulose determinations thus carried out may be taken as approximately accurate; they also exhibited fairly good agreement with each other, while, with a larger percentage of oxycellulose, differences up to 10 per cent occur. The cellulose result was 62·87 per cent; 1 grm. of the mixture evolves 23·73 c.c. NO, and from this the calculated amount of the nitrogen of the pure nitration product is 63·92 c.c. NO = 4·00 per cent N. This would correspond to a dinitrocellulose (C_{24}...) whose theoretical percentage of nitrogen is 3·96. As this stage of nitration has so far not been obtained in any other way, an attempt was made to really isolate it from the cellulose in order to determine the nitrogen directly. But all attempts with the ordinary organic solvents were unsuccessful, for the solubility is diminished by the great proportion of unchanged cellulose. We also tried, by repeatedly treating this nitration product with 1·4 nitric acid, to convert the unchanged cellulose into the desired stage of nitration, but without success. Even after the third repetition, the nitrogen percentage, and hence the amount of unchanged cellulose, remained almost constant.

On addition of 5 per cent sulphuric acid to the 1·4 nitric acid, the formation of oxycellulose is increased to nearly double the quantity. In consequence, the cellulose determination is less exact, and shows differences as great as 5 per cent. Taking the higher of the numbers thus obtained as the more correct (58·04 per cent), we obtained for the pure nitration product 81·62 c.c. NO = 5·12 per cent N. The theoretical amount of nitrogen for a trinitrocellulose (C_{24}...) would be 5·36 per cent—a stage of nitration not obtained hitherto. But this result is only an approximation, on account of the unavoidable inaccuracy of the cellulose determination. All attempts to isolate the nitration product failed.

On further addition of sulphuric acid, mixtures of nitrocelluloses with unchanged cellulose were again obtained. These experiments are given in the following table:—

Table XI.

Expt.	C.c. NO per 1 grm.	Per cent N.	Solubility in ether-alcohol.	Increase.	H_2SO_4.	HNO_3.	H_2O.
1.	147·78	9·27	14·22	134	41·86	35·82	22·32
2.	164·50	10·32	92·30	142	38·47	40·19	21·34
3.	171·57	10·76	98·24	151	40·83	38·72	20·45
4.	175·78	11·02	98·90	153	42·92	37·40	19·68
5.	195·00	12·23	99·58	155	48·03	34·18	17·79
6.	203·71	12·77	99·82	166	49·37	33·38	17·25
7.	207·70	13·02	99·32	165	50·71	32·50	16·79
8.	209·10	13·11	7·65	167	52·81	31·27	15·92
9.	214·62	13·45	2·63	173	54·92	30·06	15·02

The ratio of the cellulose to the nitric acid contained in the nitration mixture was 1:25. No unchanged cellulose was discoverable in polarised light in the product obtained in Experiment 1; but no certain conclusion could be drawn from this observation, as the greater part of the structure of the cellulose was destroyed. With iodine and sulphuric acid a brown colouration was next produced, and gradually a feeble blue; therefore it appeared that a small quantity of cellulose was still present. The nitrogen determination gave 147·78 c.c. NO. For isolation of the pure product we made use of a property of the nitration stages below octonitrocellulose discovered by Dr. Brönnert, viz., their solubility in 95 per cent alcohol containing 4 per cent calcium chloride. With this mixture, about 10 per cent was extracted in the cold, and a further amount of 35 per cent with an inverted condenser. The product showed a nitrogen content of 148·68 c.c. NO, differing only by 0·07 per cent from that of the original material. Hence only traces of cellulose could have been present. The portion insoluble in ether-alcohol contained a percentage of nitrogen corresponding to hexanitrocellulose—another proof of the insolubility of this stage of nitration.

Experiments 2—5 include the group of the collodion-cottons, *i.e.*, the stages of nitration between hepta- and enneanitrocellulose.

Experiment 6 gave a product whose nitrogen corresponded exactly to that of decanitrocellulose, and completely soluble. The question has often been raised as to the solubility of this stage of nitration. Eder considers it soluble, Vieille insoluble, and Lunge and Weintraub only obtained an insoluble decanitrocellulose. Thus we see that in this simple manner the question of the solubility of any product of nitration cannot be answered, and the percentage of nitrogen alone affords no definite conclusion as to the solubility in general. The numerous contradictory reports as to the solubility of certain stages of nitration partly originate from products falsely called nitrocelluloses, viz., those whose production is preceded by a

* *Zeitschrift fur Angewandte Chemie*, 1901, Heft 20.

solution in acid, or which are obtained by the breaking down of higher stages with alcoholic potash. But, apart from these products, we find still further complications, even in the usual method of nitration with nitric and sulphuric acid at the ordinary temperature. The decanitrocellulose obtained by Vieille by nitrating with pure concentrated nitric acid is insoluble, as also that prepared by Lunge and Weintraub with concentrated nitric-sulphuric acid 10 : 1, while that resulting from Experiment 6, obtained by using a more dilute acid mixture, is soluble. Therefore two forms of decanitrocellulose exist—the soluble and the insoluble.

This is in agreement with the researches of Sir Henry Roscoe, who, by means of the well-known cordite processes, obtained a soluble and insoluble nitro-cellulose with 12·8 per cent N.

Experiment 7 shows that it is not possible to go further in this direction; it yields a nitration product with a nitrogen content of 207 7 c.c. NO, and completely soluble. Soluble products corresponding to decanitrocellulose and higher have also been obtained on the large scale. These are of value in the manufacture of explosive gelatin and other explosive materials, with which it is important to get soluble nitration products with the highest possible percentage of nitrogen. But we see from a conference of the New York section of the Society of Chemical Industry that the conditions for obtaining these highly nitrated soluble products are not universally known; for, on the one hand, a soluble nitrocellulose with 12·9 per cent nitrogen prepared a few months previously is announced as a novelty, and on the other hand, it is asserted that this is accompanied with difficulties.

On further addition of sulphuric acid the solubility quickly diminished. Experiment 9 gave an eleven-fold nitrated cellulose. This result is very remarkable, because the nitration mixture used contained 15 per cent water, and the endecanitrocellulose formerly prepared could only be obtained with concentrated acid mixtures. We thus had cause to proceed further in this direction and obtained higher stages of nitration.

(To be continued).

ON THE METEORIC STONES WHICH FELL NEAR ZOMBA, BRITISH CENTRAL AFRICA, ON JANUARY 25TH, 1899. WITH NOTES ON THE CHEMICAL ANALYSIS OF SUCH BODIES.*

By L. FLETCHER, M.A., F.G.S.,
Keeper of Minerals in the British Museum.

(Continued from p. 83).

Unattracted Material: Third Portion.

35. THE trace of undecomposed material which, after treatment with hydrofluoric and sulphuric acids weighed 0·0026 (§ 12), must before that treatment have weighed 0·0032 (§ 19); and the total amount of undecomposed material is 0·0032+0·8107+0·0241, or 0·8380, for the undecomposed material is not appreciably altered in weight by ignition (§ 18).

The true SiO_2 is thus 0·4208−0·0032 or 0·4176; but of this, 0·0049 is due to the sodic solution itself (§ 13); hence the SiO_2 really due to the silicate is 0·4127.

The Fe_2O_3,Al_2O_3,SiO_2 0·0069 consists of Fe_2O_3 0·0037, Al_2O_3 0·0031 (SiO_2 0·0001, making the total SiO_2 0·4128).

Deducting Fe_2O_3 0·0009 as due to the sodic solution itself, Fe_2O_3 0·0028 has passed into the sodic solution from the silicate (possibly through finely-divided silicate passing through the pores of the filter).

The Fe_2O_3,Al_2O_3,SiO_2 0·3775 consists of Fe_2O_3 0·3755, Al_2O_3 0·0002 (SiO_2 0·0018, due to the action on the vessels).

CuS (ignited) 0·0003 and Ni(Co) 0·0010 may be neglected during the calculation.

MnS 0·0056 corresponds to MnO 0·0046.

The $Mg_2P_2O_7$ (pure) is 1·0958 (§ 12)−0·0054 (§ 20) or 1·0904, corresponding to MgO 0·3948.

The total Fe_2O_3 is 0·3755+0·0028 or 0·3783, corresponding to FeO 0·3405; further, 2·0317 of the unattracted material contain an amount of sulphur (§ 7) corresponding to FeS (troilite) 0·1145 which itself corresponds to FeO 0·0936; as this iron is in the acid solution, only 0·3405−0·0936, or 0·2469, of FeO is due to the silicate.

The total CaO obtained is 0·0023+0·0107 or 0·0130; from this must be deducted 0·0005 as due to the sodic solution (§ 13).

Also 2·0317 of the unattracted material contain (§ 32) K_2O 0·0017, Na_2O 0·0241; and the 0·8380 of undecomposed material contains (§ 22) K_2O 0·0015, Na_2O 0·0133; hence K_2O 0·0002 (or nil) and Na_2O 0·0108 must have passed into the acid and sodic extracts.

Collecting these results we have:—

		Percentages.
Undecomposed material	0·8380	41·25
Troilite	0·1145	5·64
SiO_2	0·4128	20·32
FeO	0·2469	12·15
MnO	0·0046	0·23
MgO	0·3948	19·43
CaO .. { Acid extract 0·0107 / Sodic extract 0·0018 } ..	0·0125	0·61
Al_2O_3 { Acid extract 0·0002 / Sodic extract 0·0031 } ..	0·0033	0·16
K_2O	Nil	Nil
Na_2O	0·0108	0·53
Total	2·0382	100·32
Weight taken ..	2·0317	100·00

36. Bringing the results together for convenience of comparison, we have—

	I.	II.	III.	Mean.	Oxygen.	
Undecomposed material ..	42·13	43·21	41·25	42·20	—	
[Troilite	5·63	5 64	5·64	5·64]	—	
SiO_2	19·33	19·65	20·32	19·77	10·47	
FeO	11·83	12·06	12·15	12·01	2·67	10·46
MnO	0·22	0·23	0·23	0·23	0·05	
MgO	Undet.	18·72	19·43	19·07	7·59	
CaO	Undet.	0·42	0·61	0·51	0·15	
Al_2O_3	0·19	0·20	0·16	0·18	0·08	
[Na_2O	Undet.	0·50	0·53	0·51]	0·13	
Total	79·33	100·63	100·32	100·12		
Weight taken	100·00	100·00	100·00	100·00		

In the analysis of the first portion, the three successive extractions with acid were allowed to proceed for one and a-half hours, two hours, and two hours respectively; in the case of the second portion the times were two hours, one and three-quarter hours, and two hours respectively; in that of the third portion, each extraction lasted two hours. As it has been shown (§ 30) that no less than 11·64 per cent of the undecomposed material are decomposed during such extractions, it follows that the variation from 41·25 per cent to 43·21 per cent in the amount of residue in the three analyses is sufficiently accounted for by variations of circumstances during the extractions; for instance, of the times for which each extraction is allowed to proceed, the temperature of the extracting acid, the frequency of renewal of the evaporated water, and so on. The actual extract corresponds very closely to olivine, and, neglecting the soda and alumina, has the following composition:—

* From the *Mineralogical Magazine*, vol. xiii., No. 59, 1901.

	Per cent.		Oxygen.		Muddoor.	Linn County.
SiO_2 ..	19·77	38·25	20·26		38·32	38·80
FeO ..	12·01	23·23	5·16	20·28	23·29	21·31
MnO ..	0·23	0·45	0·10		—	—
MgO ..	19·07	36·89	14·68		36·90	39·89
CaO ..	0·51	1·18	0·34		1·07	—
Al_2O_3 .	—	—	—		0·42	—
	51·59	100·00			100·00	100·00

This composition is virtually identical with that calculated by Crook (" Die Chemische Natur der Meteoriten," von C. Rammelsberg, 1879, p. 54) for the olivine of the Muddoor meteorite, and also is very nearly that of the " decomposed portion " of the Linn County stone as analysed by Rammelsberg (*Monatsb. Ak. Wiss. Berlin*, 1870, p. 459).

Some of the silica, however, must have been originally in combination with the soda and alumina which have been neglected, and further a small quantity of the remaining constituents is due to the action of the hydrochloric acid and sodic solution on the enstatitic silicate.

37. An estimate of the quantities due to the action on the refractory silicates can be obtained by assuming that they are in the same proportion to the undecomposed residue as in the analysis mentioned in § 30. But the estimate will be only approximate, for in the analysis of the mixture the strength of the acid and its decomposing effect are diminished owing to the action of the olivine; further, the gelatinous silica from the olivine will partially protect the other silicates from the acid; and the presence of the compounds due to the decomposition of the olivine may have a disturbing effect on the action of the acid.

These considerations being disregarded, it follows from § 30 that when the residue weighs 88·36 the following amounts due to the refractory silicates have passed into solution:—SiO_2 6·57, FeO 1·20, MgO 2·03, CaO 0·93, Al_2O_3 0·67, R_2O 0·24; hence for the residue, 42·20, the corresponding amounts are—SiO_2 3·14, FeO 0·57, MgO 0·97, CaO 0·44, Al_2O_3 0·32, R_2O 0·11, making in all 5·55. Deducting these amounts from the quantities found in the solution (§ 36), we have for the less refractory silicate itself:—SiO_2 16·63, FeO 11·44, MnO 0·23, MgO 18·10, CaO 0·07, Al_2O_3 —0·14, Na_2O 0·40. Omitting the CaO, Na_2O, Al_2O_3 as being possibly extraneous, we have the following composition:—

	Per cent.		Oxygen.		Muddoor (observed).
SiO_2 . ..	16·63	35·84	18·98		35·46
FeO . ..	11·44	24·65	5·48	21·11	24·36
MnO ..	0·23	0·50	0·11		—
MgO ..	18·10	39·01	15·52		38·61
CaO . ..	—	—	—		1·13
Al_2O_3 ..	—	—	—		0·44
	46·40	100·00			100·00

The nearness of the oxygen ratio to that of olivine is thus lessened by the deduction of the quantities resulting from the action on the refractory silicates; but the composition is almost identical with that observed by Crook for the decomposable silicate of the Muddoor meteorite.

According to this interpretation, the total amount of enstatite, felspar, and chromite in the unattracted material would be 47·75 per cent, 42·20 per cent remaining undecomposed and 5·55 per cent passing into the acid and sodic solution.

Unattracted Material: Chromite.

38. Since the unattracted material yields 42·20 per cent of undecomposed residue (§ 36), and the latter itself contains (§ 28) 1·45 per cent of chromite, the unattracted material must contain 0·61 per cent of chromite. By direct extraction with hydrofluoric and sulphuric acids only 0·35 per cent was isolated, but probably some is decomposed and passes into solution (§ 6). Similarly, the chromium obtained during the determination of the alkalis corresponds to only a small fraction of the total chromite (*Mineralogical Magazine*, 1894, x., 307).

39. The enstatite and oligoclase of the unattracted material will thus (§§ 37, 38) amount to (47·75—0·61 or) 47·14 per cent, and this will consist (§ 28) of 37·65 of enstatite and 9·49 of oligoclase; the troilite is 5·64 per cent (§ 36); hence the olivine amounts to 46·61 per cent. The mineral composition of the unattracted material (neglecting minute quantities of nickel-iron and schreibersite) will therefore be—

		Total weight. Grms.
Olivine	46·61	5·7894
Enstatite	37·65	4·6764
Oligoclase	9·49	1·1787
Troilite	5·64	0·7005
Chromite	0·61	0·0758
	100·00	12·4208

(To be continued).

THE ESTIMATION OF CARBONIC ACID IN WATER.*

By JOSEPH W. ELLMS and JAY C. BENEKER.

(Continued from p. 81).

Pettenkofer's and Trillich's Methods.

The estimation of the carbonic acid in natural waters consists in determining the amount of half-bound and free carbonic acid which may be present. The estimation of the fixed carbonic acid is generally regarded as a separate determination, and is not commonly included in the statement of the results.

The principle upon which Pettenkofer based his determination depends on the action which the barium or calcium hydroxide has upon free and half-bound carbonic acid, whereby insoluble calcium and barium carbonates are formed which precipitate out of solution. Either calcium or barium hydroxide may be used, the reactions involved being of similar character.

As an excess of the precipitant is used, the portion unacted upon is determined volumetrically with a standard acid solution, and the amount of the barium or calcium hydroxide which has reacted with the free and half-bound carbonic acid can thus be determined by difference. The reaction is as follows:—

$$Ca(HCO_3)_2 + CO_2 + 2BaO_2H_2 = 2BaCO_3 + CaCO_3 + 2H_2O.$$

As the calcium carbonate present has been held in solution by the assistance of the half-bound molecule of carbon dioxide, it also precipitates upon the latter's removal by the barium hydroxide.

In so far as that portion of the half-bound carbonic acid, which may be present in a natural water, is combined with the magnesium carbonate to form the bicarbonate, the reaction between it and the calcium or barium hydroxide is the same as shown by the above reaction. But magnesium carbonate ($MgCO_3$) instead of precipitating out as such, reacts with the calcium or barium hydroxide and forms magnesium hydroxide, which latter, being insoluble, precipitates. The presence, therefore, of magnesium carbonate—or, in fact, any magnesium salt—causes the calcium or barium hydroxide to be used up. Pettenkofer avoids the precipitation of the magnesium by the introduction of ammonium chloride, which, by forming a soluble salt of ammonium and magnesium chloride, prevents any loss of calcium or barium hydroxide. The reaction is as follows:—

$$MgCO_3 + 4NH_4Cl + BaO_2H_2 = MgCl_2(NH_4Cl)_2 + BaCO_3 + 2NH_4OH.$$

* *Journal of the American Chemical Society*, xxiii., No. 6.

An equivalent amount of ammonium hydroxide being formed, no change in the caustic alkalinity of the sample results.

Trillich's modification of Pettenkofer's method consists in not attempting to prevent the reaction between the magnesium salts and the caustic alkali by the addition of ammonium chloride, but in allowing the precipitation to take place. From a direct gravimetric determination of the amount of the magnesium present in another portion of the sample, he is enabled to apply the proper correction to the result obtained volumetrically. Since 40 parts of magnesium oxide (MgO) would react with as much barium or calcium hydroxide as 44 parts of carbon dioxide, the correction is obtained by multiplying each part of magnesium oxide (MgO) present by 1·1 and subtracting the product from the apparent amount of carbonic acid found by the volumetric determination. Trillich's method, therefore, only differs from the original Pettenkofer method in providing another way to overcome the difficulty arising from the presence of magnesium salts.

In order to differentiate between the free, half-bound, and fixed carbonic acid, Trillich uses that portion of his solution which contains the precipitated carbonates, and titrates it with hydrochloric acid and cochineal. From this he obtains the "total carbonic acid." By subtracting the "free and half-bound carbonic acid" from this, he obtains the "fixed carbonic acid"; and by finding the difference between the "free and half-bound acid" and the "fixed" (equivalent to the half-bound), he estimates the "free carbonic acid."

It is apparent that by this means the various forms of carbonic acid may be determined in Pettenkofer's method, although the writers are not aware that originally any such differentiation was attempted. Moreover, it would seem more simple to use a method which would not involve the objectionable titration of the suspended carbonates and magnesium hydroxide. This can be done by determining the fixed carbonic acid by direct titration of a separate sample of the water by Hehner's method, and from this all the data given can easily be deduced. In our examination of these methods we have not attempted to carry out Trillich's titration of the portion of the sample containing the precipitated carbonates.

In Pettenkofer's method and in Trillich's as well, oxalic acid is used to titrate the excess of the barium or calcium hydroxide added to the water under examination. If barium hydroxide is used, Trillich recommends that to each 9 grms. of the barium hydroxide, 0·5 grm. of barium chloride be added in order to convert the hydroxides of sodium and potassium, which are common impurities of barium hydroxide, into chlorides. The reason for this and for the addition of barium or calcium chloride in the original Pettenkofer method, is more fully stated by Fresenius as follows ("Quantitative Chemical Analysis," p. 405, English edition, 1889):—

"If . . . a water contains an alkali carbonate or any other alkali salt whose acid would be precipitated by lime or baryta, a neutral solution of calcium or barium chloride must be added to decompose the same. This addition, too, prevents any inconvenience arising from the presence of free alkali in the lime or baryta water, or of magnesium carbonate in the carbonic acid water; this inconvenience consists in the fact that oxalate of an alkali or of magnesium enters into double decomposition with calcium carbonate (which is seldom entirely absent from the fluid to be analysed), forming calcium oxalate and carbonate of the alkali or of magnesium, which latter will of course again take up oxalic acid."

The details of the Pettenkofer process consist in taking 100 c.c. of the water to be analysed, placing it in a bottle, adding 3 c.c. of barium chloride, 2 c.c. of a saturated solution of ammonium chloride, and 45 c.c. of barium hydroxide solution. After allowing the mixture to stand about twelve hours closely stoppered, an aliquot portion of the clear supernatant liquid is pipetted off and titrated with oxalic acid. In our experiments, an approximately 0·02 normal solution of sulphuric acid was used. The barium hydroxide solution was approximately 0·05 normal and the indicator employed was rosolic acid.

The Trillich method differs from the above in using 5 c.c. of barium chloride in place of 3 c.c., omitting the ammonium chloride, and using phenolphthalein as the indicator. In titrating the suspended carbonates for the determination of the total carbonic acid, Trillich employs hydrochloric acid and cochineal as the indicator, as previously stated.

In carrying out these methods the following precautions have been found necessary in order to obtain uniform and consistent results:—

1. The barium hydroxide solution (9 grms. $BaO_2H_2.8H_2O$ and 0·5 grm. $BaCl_2.2H_2O$ per litre) should be carefully filtered and kept in a bottle whose outlet to the air is provided with a U-tube containing fused calcium chloride and stick potash. A syphon tube conveniently conveys the liquid to the measuring burette. Solutions thus protected will keep for a long time without serious deterioration. A solution thus guarded from the atmospheric carbon dioxide was found at the end of fifty days to be 0·6 per cent weaker than when first tested.

2. If oxalic acid is used, it should be frequently tested, as it deteriorates rapidly. A solution containing 2·8636 grms. per litre (1 c.c. = 1 m.grm. CO_2) was found at the end of forty-five days to be 6·7 per cent weaker, and one fifty days old was 8·7 per cent weaker.

3. Dry or well drained ground-glass stoppered bottles, with their stoppers well vaselined, should be used for holding the samples. On account of the strong tendency which barium hydroxide solutions exposed to the air show in the absorption of atmospheric carbon dioxide, the most erratic results will be obtained if the bottle stoppers are not tight-fitting.

4. Samples of water to be analysed should properly, if at all high in free and half-bound carbonic acid, be introduced into the bottle by means of a syphon or tube, similar to the methods used in taking samples for determining dissolved oxygen.

5. After the introduction of the sample into the bottle, the other reagents should be added, the barium hydroxide solution, however, always being the last to be introduced. The barium hydroxide should be introduced by means of a long delivery tip on the burette, the lower end of which dips below the surface of the sample in the bottle. The barium hydroxide should be run in as quickly as possible, and the bottle immediately stoppered and shaken.

6. The bottle should then be set aside to stand at least twelve hours, and under no conditions should the stopper be removed until the clear supernatant liquid is pipetted off for immediate titration.

7. The removal of the 25 or 50 c.c. of the liquid to be titrated should take place without stirring up the precipitate in the bottom of the bottle. This is extremely important, and its neglect, even when only a slight amount of sediment is withdrawn, will lead to irregular and unreliable results.

8. The receptacle in which the titration takes place should be a narrow-mouthed fairly long-necked flask, preferably of about 250 c.c. capacity. The titration should take place immediately upon the withdrawal of the portion from the bottle, and the acid should be run in quickly.

9. If the delivery of the acid can be quickly effected, the larger portion should be delivered into the flask holding the barium hydroxide as soon as possible without any unnecessary shaking of the flask. The titration can then be cautiously completed. If, however, the burette delivers the acid slowly, it is better to run into the empty flask the larger portion of the acid, and then add the portion of the sample to be titrated. This avoids undue exposure of the caustic alkali to the air, and consequently any carbonating of the barium hydroxide.

10. The standardisation of the barium hydroxide solution by the acid should be carried out in a manner similar to the method employed in the titration of the sample.

In standardising the barium hydroxide solution in order to obtain its value in terms of the acid, it is necessary in the Pettenkofer method that the titration should take place in the presence of ammonium chloride, if rosolic acid, or any indicator which is at all affected by this salt, is used. Otherwise the value of the alkali in terms of the acid will be erroneous, and the differences, though slight, will lead to considerable error.

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JULY 31ST, 1901.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, August 10th, 1901.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 216 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from July 1st to July 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 216 samples examined chemically by us during July, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during the month shows an excess for the first time since April. The actual rainfall measured was 4·66 inches, of which 4·33 inches fell on the 24th, 25th, 26th, and 27th. The average fall for the month of July is only 2·49 inches; this gives an excess of 2·17 inches on the thirty-five years' average, and reduces the previous deficit for the year to 0·13 inch, or 0·9 per cent.

Our bacteriological examinations of 477 samples have given the results recorded in the following table; we have also examined 111 other samples, from special standpipes, houses, &c., making a total of 588 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	383
New River, filtered (mean of 119 samples) ..	13
Thames, unfiltered (mean of 27 samples) ..	5560
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 245 samples)..	35
Ditto ditto .. .. highest	360
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 26 samples) ..	837
River Lea, from the East London Company's clear-water wells (mean of 34 samples) ..	40

Out of the total number of samples of filtered water collected and examined, 59 samples gave such abnormally high results that they are excluded altogether, and are dealt with in our subsequent remarks.

Of the remaining 398 samples of impounded and filtered water supplied to London and examined bacteriologically during the past month, 9 samples, or 2·2 per cent, were sterile. Ten samples contained more than 150 microbes, and 31 samples, or 7·7 per cent, contained more than 100 microbes per c.c. The mean number of microbes in the excess samples was 173, against a corresponding mean of 155 in June.

We have pointed out on previous occasions that during the summer months, when the rainfall is small, the river Thames mainly consists of spring water derived from the large deposits of chalk in the upper Thames valley.

For the last six years the bacteriological examination of the London water supply has shown an exceptionally high degree of purity during the summer months, and this year also, during June and the first week of July, we have enjoyed the normal bacterial purity of the dry summer supply. But between the 6th and the 15th of July, nearly the whole of the filtered water of the different companies, derived from the valleys of the Thames and Lea, showed an excessive number of microbes per cubic centimetre, far above the variations permissible as showing the difference between good and bad filtration. After the 15th of July the supply rapidly reassumed its usual high quality.

This abnormal development of microbes in the filtered water would appear to be due to some exceptional climatic conditions, favouring, in all probability, the development of vegetable spores of a harmless character, because, after careful examination we have satisfied ourselves that there has been nothing very unusual in the general rate of filtration, the mode of taking samples, or the method of testing. The fact that this microbial outbreak was general throughout all the Companies is a proof that it could not be due to any want of care in the filtration, for it would be impossible to conceive that all the Companies simultaneously were using defective filters, or filtering at an excessive rate. Moreover, during these nine days the raw Thames, Lea, and New River waters were exceptionally good, and therefore the difficulty of dealing with their further purification should have been, with efficient supervision, less than during other times of the year.

On minute examination of the microbes we could discover none of a pathogenic character; no did we find the microbe associated with decomposing animal matter, viz., Bacillus coli communis. There were undoubtedly liquefying organisms occasionally present, and minute bacteria such as do not usually occur amongst ordinary river microbes. A similar unexplained bacterial outburst was recorded by Sir Edward Frankland and ourselves during the severe winter of 1894-5.

During the latter part of the month of July the Thames valley was visited by an exceptionally high rainfall, and in consequence the unstored, crude, Thames water has become from twelve to fifteen times worse bacterially. But in spite of this the London supplies have resumed their normal character; again proving that the microbic purity of the supply is substantially independent of the condition of the running river.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

Action of Silver on Hydrobromic Acid and the Inverse Reaction.—M. Journiaux.—An investigation of the action of silver on hydrobromic acid gives results which are in general parallel to those which the author obtained whilst examining the action of silver on hydrochloric acid. The experiments were conducted at about 600° in sealed tubes, the hydrogen being under varying pressures. The influence of temperature on the limits of the two inverse reactions $Ag + HBr \lesssim AgBr = H$ was examined, the limits of temperature being 0° and 700°.—*Comptes Rendus*, cxxxiii., No. 4.

THE DISSOCIATING POWER OF DIFFERENT SOLVENTS.*

(A Summary).

By HARRY C. JONES.

The question of the dissociating power of different solvents is one of the most important in physical chemistry to-day. The first step in the study of the physical chemistry of any solvent is to determine accurately its dissociating power, in order that the knowledge obtained may not be simply qualitative but quantitative.

It has often been pointed out that physical chemistry, until quite recently, was almost exclusively the physical chemistry of aqueous solutions. This is due to the fact that water is a good solvent for many substances, that it can be easily obtained in a high degree of purity, and kept free from other solvents, and further, that the dissociating power of water can be easily measured. In the last yew years, however, a beginning has been made with other solvents, and the first step—the measurement of their dissociating power—taken, at least approximately in a number of cases.

The question of the dissociating power of solvents has acquired additional interest because of certain theories which have been proposed, connecting this property of solvents with other properties, chemical and physical. Thus, J. J. Thomson (*Phil. Mag.*, xxxvi., 320), and also Nernst (*Zeit. Phys. Chem.*, xiii., 531), have proposed the theory that the dissociating power of solvents should be very closely connected with their dielectric constants. Brühl (*Zeit. Phys. Chem.*, xviii., 514; xxvii., 319; xxx., 1; *Ber. d. Chem. Ges.*, xxx., 163; xxviii., 2847; and xxviii., 2866), thinks that water and similar substances are non-saturated compounds, and refers the large association of their molecules (shown by the surface-tension method of Ramsay and Shields), as well as their large dielectric constant and high dissociation power, to this cause. Ciamician (*Zeit. Phys. Chem.*, vi., 403), thinks that dissociation is a chemical function of the substance, and those compounds which resemble one another chemically, as water, methyl alcohol, &c., should have the greatest dissociating power. While Konowalow (*Wied. Ann.*, xlix., 733), holds the opinion that only those solutions conduct where there is a chemical action between the solvent and the dissolved substance.

The work which has been done will be considered under the following heads:—Inorganic solvents, organic solvents, and mixed solvents.

Inorganic Solvents.

Water.—The dissociating power of water has been determined for a large number of substances, by several different methods. The more general methods are:—The conductivity method of Kohlrausch (*Wied. Ann.*, xxvi., 160), and the solubility method of Nernst (*Zeit. Phys. Chem.*, iv., 372), and Noyes (*Zeit. Phys. Chem.*, vi., 241,; ix., 603; xii., 162; xvi., 125), and the freezing-point methods of Jones (*Zeit. Phys. Chem.*, xi., 110, 529; xii., 623), Loomis (*Wied. Ann.*, li., 500; lvii., 495, 591; lx., 523), and others.

The results obtained by all of these methods agree to within the limit of experimental error. Water, as we shall see, has the highest dissociating power of any solvent thus far obtained in the pure state, and it is probable that there is only one other substance known which, under similar conditions, can ionise substances to the same extent as water.

To determine the dissociating power of solvents other than water, the conductivity method has thus far been chiefly used. In order that the conductivities in other solvents may be compared with those in water, the results for a typical acid, base, and salt in aqueous solution are given. The following measurements were made at 18°. The volume v is the number of litres which contains a grm.-molecular weight of the electrolyte. μ_v is the molecular conductivity at the volume v.

Hydrochloric acid.		Potassium hydroxide.		Potassium chloride.	
v.	μ_v.	v.	μ_v.	v.	μ_v.
0·1	60·0	0·1	42·3		
0·2	142·0	0·2	99·0		
0·333	201·0	0·333	131·4	0·333	82·7
1·0	278·0	1·0	171·8	1·0	91·9
10·0	324·4	10·0	198·6	10·0	104·7
100·0	341·6	100·0	212·4	100·0	114·7
500·0	345·5	500·0	214·0	500·0	118·5
1000·0	345·5	1000·0	213·0	1000·0	119·3
				5000·0	120·9
				10000·0	120·9

The percentage of dissociation, α, at any dilution is obtained by dividing the value of μ_v at that dilution by the maximum value of μ_v for the substance which is called μ_∞.

In most solvents it is impossible to determine the value of μ_∞ directly by the conductivity method, since the dilution at which μ_∞ is reached would be so great that it would not be practicable to apply the conductivity method to it. The best that can be done in such cases is to determine the values of μ_v for varying dilutions and then compare these with the corresponding values in water. In this way an approximate idea of the dissociating power of different solvents can be obtained.

Ammonia.—That solutions of salts in liquid ammonia conduct the current was shown several years ago by Cady (*Journ. Phys. Chem.*, i., 707). Goodwin and Thompson (*Phys. Rev.*, viii., 38), also made some measurements of the conductivity of such solutions, in connection with their work on the dielectric constant of liquid ammonia, but the most elaborate investigation in this field is that of Franklin and Kraus (*Amer. Chem. Journ.*, xxiii., 277; xxiv., 83). They measured the conductivity of potassium bromide and nitrate, sodium bromide and bromate, ammonium chloride and nitrate, silver iodide and cyanide, mercuric cyanide, and a number of organic compounds in liquid ammonia, at dilutions ranging from a few hundred to many thousand litres. A few of their results for three salts are given:—

Potassium bromide.		Ammonium chloride.		Silver iodide.	
v.	μ_v.	v.	μ_v.	v.	μ_v.
301·9	210·6	298·9	159·0	314·1	83·5
932·6	259·5	923·4	208·7	951·3	122·7
4099·0	308·5	4059·0	264·7	4034·0	188·2
21480·9	336·1	21270·0	298·8	18200·0	247·5
65040·0	340·2	64400·0	301·4	55120·0	274·0
78430·0	340·4	77660·0	304·4	80000·0	276·0

A direct comparison of the molecular conductivities of salts in liquid ammonia with the molecular conductivities in water at the same dilutions, will show that the former values are much larger than the latter. This would seem to indicate, at first sight, that ammonia has a greater dissociating power than water, but such is not the case. It will be observed that the conductivities in water are measured at 18°, or 82° below its boiling-point, while the conductivities in liquid ammonia are measured at its boiling-point −38°. The conductivities in liquid ammonia should be compared with the conductivities in water at its boiling-point, and the latter values would be, in many cases, more than double the conductivities in water at 18°.

Further, if the molecular conductivities in liquid ammonia should even be greater than in water under comparable conditions, this alone would not show that the

* *American Chemical Journal*, xxv., No. 3.

dissociating power of ammonia was greater than that of water. The percentage of dissociation,

$$\alpha = \frac{\mu_v}{\mu_\infty};$$

μ_v might be larger in ammonia than in water, and the difference between the two values of μ_∞ might be even greater, so that μ_∞ would be smaller in ammonia. Such is the fact. The high value of the molecular conductivity in ammonia is due rather to the great velocity with which the ions move through this solvent than to the large number of ions present.

Nitric Acid.—Bouty (*Comptes Rendus*, cvi., 595), has shown that the conductivity of certain alkaline nitrates dissolved in nitric acid is very large, being of nearly the same magnitude as in water. The work is far too incomplete to enable us to draw any conclusion as to the relation between the dissociating power of nitric acid and of water. The dissociating power of the acid is, probably, very great.

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 5, July 29, 1901.

The Solubility of Mixtures of Copper Sulphate and Sodium Sulphate.—MM. Massol and Maldés.—Solutions obtained from a mixture of copper sulphate and sodium sulphate (both salts being in excess) possess an invariable composition at low temperatures, as Rüdorff has already observed, but when the temperature is high enough for the anhydrous modification of sodium sulphate to be formed (from 23—32° according to the nature of the mixture) the composition of the solution varies with the relative proportions of the two salts.

Neodymium Chloride.—Camille Matignon.—Will be inserted in full.

Alloys of Aluminium and Molybdenum. — Leon Guillet.—By the reduction of molybdic acid with aluminium, six compounds can be isolated corresponding to the formulæ Al_7Mo, Al_3Mo, Al_2Mo, $AlMo$, $AlMo_2$, and finally a compound very rich in molybdenum which apparently corresponds to the formula $AlMo_{20}$. The author examines the properties of all these compounds.

Crystallisation of Cerium Oxide.—Jean Sterba.—By a method of crystallisation of cerium oxide at different temperatures the author obtained this substance in cubes or cubo-octahedrons, isotropic, colourless, and transparent, but whose density varies according to the temperature at which crystallisation takes place.

Cæsium.—C. Chabrié.—In order to obtain all the metal from the mineral containing cæsium the author suggests the plan of drying the mineral at 130°, grinding it to a fine powder, and reducing it in a platinum crucible with a hundred times its weight of pure hydrofluoric acid. The whole must be brought to boiling point and kept at that temperature until solution is nearly complete. The partial solution is then filtered, and after transformation into carbonate can be evaporated to dryness. The author also obtains in a pure state cæsium sulphite, bisulphite, and hyposulphite.

Pyrogallol Sulphonic Acids.—Marcel Delage.—The author devises a method for the estimation of pyrogallol di- and mono-sulphonic acids, using phenolphthalein as an indicator. He also prepares by double decomposition, between a molecule of a metallic sulphate and a molecule of the barium salt, potassium pyrogallol-monosulphonate, $C_6H_2(OH)_3SO_3K+2H_2O$, sodium pyrogallol-monosulphonate, $C_6H_2(OH)_3SO_3Na+2H_2O$, ammonium pyrogallol-monosulphonate, $C_6H_2(OH)_3SO_3(NH_4)+H_2O$, potassium pyrogallol-disulphonate, $C_6H(OH)_3(SO_3K)_2+H_2O$, sodium pyrogallol-disulphonate, $C_6H(OH)_3(SO_3Na)_2+3\frac{1}{2}H_2O$, and ammonium pyrogallol-disulphonate—

$$C_6H(OH)_3(SO_3{-}NH_4)_2+2H_2O;$$

also aluminium and magnesium pyrogallol-disulphonate.

Action of Ethylic Alcohol on Barium Ethylate. Synthesis of Normal Butylic Alcohol.—Marcel Guerbet.—Will be inserted in full.

MISCELLANEOUS.

Action of Cupric Hydrate on Solutions of Metallic Salts.—A. Mailhe.—Tetracupric hydrate always gives a mixed basic salt when placed in contact with one of the solutions of chlorides or bromides of the metals mercury, zinc, manganese, cobalt, nickel, cadmium, and lead. The action is slow in the cold, but becomes much more rapid on heating. Several minutes of contact are necessary for the action to be complete. The author intends to investigate the analogous reactions of cupric hydrate on solutions of metallic sulphates and nitrates. — *Comptes Rendus*, cxxxiii., No. 4.

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THE CHEMICAL NEWS.

VOL. LXXXIV., No. 2179.

CHLORIDE OF NEODYMIUM.

By CAMILLE MATIGNON.

PURE neodymium chloride, crystallised with $6H_2O$, was first prepared by Schapleigh and exhibited in the Chicago Exhibition. This substance forms the chief constituent of old neodymium chloride. It is deposited from its hydrochloric solution at ordinary temperatures under the same form, $NdCl_3.6H_2O$

This chloride is deposited in large, deliquescent, clinorhombic, rose-coloured crystals, of density at 16·5° C. = 2·282 and with a molecular volume equal to 156·9.

Chloride of neodymium is very soluble in water. At 13°, 100 parts of water dissolve 246·2 parts of the hydrated salt, or 98·7 parts of the anhydrous salt; 100 parts of the solution contain 49·6 parts of the anhydrous salt and 71·1 parts of the crystallised salt; this solubility increases with the temperature. At 100°, 100 parts of water dissolve 511·6 parts of the hydrated salt and 140·4 parts of the anhydrous salt; whilst 100 parts of the solution contain 58·4 grs. of the anhydrous salt or 83·6 grs. of the hydrated salt.

The saturated solution at 13° has a density equal to 1·741.

The chloride dissolves in water with evolution of heat. Two experiments made with the chlorides dissolved in water and in hydrochloric acid give respectively the values +7·58 cal. and +7·64 cal. at 14°:—

1. $NdCl_3.6H_2O$ sol. + Aq = $NdCl_3$ diss. + 7·60 cal.

The concentrated solution of chloride possesses the property of dissolving neodymium oxalate easily, and the insoluble oxalates of the other rare earths. On cooling the hot solution, we obtain crystals of oxalo-chlorides, salts whose composition was found by M. Job (*Comptes Rendus*, cxxvi., p. 246). It is impossible to dry the hydrated chloride in the air-oven without a certain amount of transformation into the oxychloride, but decomposition does not take place when desiccation is effected in a current of dry hydrochloric acid gas. Heated under these conditions to 105°, the chloride slowly loses $5H_2O$, after which dehydration stops. We have then a new monohydrated chloride, $NdCl_3H_2O$.

At 130°, the chloride $NdCl_3H_2O$ keeps its water even in dry hydrochloric acid gas, and a temperature above 160° must be attained for the last molecule of water to disappear, and a pure anhydrous salt to be obtained containing no oxychloride.

A very simple method can be devised for preparing anhydrous neodymium chloride—a chloride which was recently prepared by MM. Muthmann and Stützel (*Berichte*, xxxii., p. 3413) by first transforming the sulphate into sulphide in a current of sulphuretted hydrogen, then the sulphide into anhydrous chloride by the medium of hydrochloric acid gas. By this means I easily prepared more than 500 grms. of the anhydrous chloride. The substance thus obtained is in the form of a rose-coloured powder, extremely deliquescent, which melts at a red heat to a liquid, which liquid, on cooling, becomes a rose-coloured transparent mass. It is not perceptibly volatile at a temperature of 1000—1100°. When thrown into water, the anhydrous chloride dissolves with a hissing noise, like hot iron. The heat evolved at the moment of solution has been found equal to +34·80 cal. at a temperature of 16°:—

2. $NdCl_3$ + Aq = $NdCl_3$ diss. + 34·8 cal.

By combining the two Equations, 1 and 2, we can deduce the heat of formation of the hydrated salt from the anhydrous salt:—

$NdCl_3$ sol. + $6H_2O$ sol. = $NdCl_3.6H_2O$ sol. + 18·8 cal.

Absolute alcohol dissolves the anhydrous chloride abundantly. I utilised this property to determine the molecular mass by the variation of the boiling-point of this solvent. Three experiments gave the following values, using the formula $M = K\frac{P}{E}$, where K = 11·5.

	E. c	P. Grs.	M.
I.	0·127	2·74	248
II.	0·154	3·12	233
III.	0·557	11·11	230

The molecular mass for the formula $NdCl_3$ is equal to 250 (Nd=143·5). The formula $NdCl_2$ with Nd=95·6 would give a molecular mass equal to 166·6. The formula of neodymium is therefore $NdCl_3$ if we admit that the quantity of neodymium combined with three atoms of chloride represents a single atom of neodymium.

This hypothesis can be verified by a determination of the lowering of the freezing-point of water containing a small quantity of the chloride in solution. Three experiments have given the following values:—

	Weight of $NdCl_3.6H_2O$ in 100 parts water.	Lowering observed.	Molecular lowering (M=3·58).
I.	3·426	0·565	59·2
II.	2·967	0·50	60·3
III.	1·262	0·230	65·5

From these results the limit of molecular lowering should be about 66 or 67. This value corresponds exactly to salts consisting of three monovalent acid radicles united to a trivalent metallic radicle. Raoult found, for example, the following limits for salts of the same constitution:—$AlCl_3$, 64·5; $CrCl_3$, 65; $(NO_3)_3Al$, 65·4. Consequently, the molecule of neodymium chloride contains a single atom of neodymium; all the other possible hypotheses do not agree with the preceding numbers. Summing-up the above, I have (1) determined the principal physical constants of neodymium chloride, (2) discovered a new hydrate $NdCl_3.H_2O$, (3) given a simple method of preparation by means of anhydrous neodymium chloride, (4) shown that neodymium is trivalent in its chloride, and that its atomic mass corresponds to the quantity of metal in this body united to three atoms of chlorine. I may finally add that I have been able to isolate the metal itself by the action of sodium on the anhydrous chloride.—*Comptes Rendus*, vol. cxxxiii., No. 5.

ACTION OF ETHYLIC ALCOHOL ON BARIUM ETHYLATE.

SYNTHESIS OF NORMAL BUTYLIC ALCOHOL.

By MARCEL GUERBET.

I HAVE already read a paper before the Académie, describing the preliminary results of my researches on a new method of synthesis of alcohols, founded on the reaction which takes place at 200° between the alcohols and their sodium derivatives (*Comptes Rendus*, vol. cxxviii., p. 511 and 1002; and vol. cxxxii., p. 207 and 685). At this temperature a molecule of sodium is eliminated between these compounds and an alcohol is formed, which is twice condensed from the original alcohol; the reaction can be expressed in the following manner:—

$C_nH_{2n+1}ONa + C_nH_{2n+1}OH = C_{2n}H_{4n+1}OH + NaOH.$

The soda thus produced reacts immediately on the alcohols, transforming them partially into the sodium salts of the corresponding acids, with evolution of

hydrogen. We thus obtain, with isoamylic alcohol $C_5H_{12}O$; diamylic alcohol, $C_{10}H_{22}O$, and isovaleric acid; with œnanthylic alcohol, $C_7H_{16}O$; dicœnanthylic alcohol, $C_{14}H_{30}O$, and œnanthylic acid; with caprylic alcohol, $C_8H_{18}O$; dicaprylic alcohol, $C_{16}H_{34}O$, and caprylic acid. Ethylic alcohol, C_2H_6O, is apparently an exception, because when heated to 210° with its sodium derivative we do not obtain butylic alcohol, $C_4H_{10}O$, as might be expected, but ethylene.

The elimination of the soda, instead of being effected between the alcohol and its sodium derivative as in the case of alcohols of higher atomicity, is simply effected by the sodium ethylate, $C_2H_5ONa = C_2H_4 + NaOH$. I thought that the general reaction, which does not take place with sodium ethylate, might be produced perhaps with barium ethylate, and experiment has confirmed my hypothesis. By heating a concentrated solution of barium ethylate in absolute alcohol to 230° or 240° a small quantity of normal butylic alcohol is produced at the same time as ethylene and hydrogen, besides some acetate and carbonate of baryta. The concentrated solution of barium ethylate is prepared by the method recommended by M. Berthelot (*Annales de Chemie et de Physique*, Series 4, vol. xxx., p. 142). The caustic baryta is dissolved in absolute alcohol in the cold, and the solution brought to boiling-point.

The barium ethylate, less soluble in hot than in cold alcohol, is precipitated and falls to the bottom. The larger portion of the alcohol is now poured off, and the required concentrated solution obtained. This was used for my experiments, and contained 28·5 parts per 100. The solution is divided up into tubes which are sealed, and then heated to 230—240° for three days. Each twenty-four hours the tubes are opened to allow the gas to escape, and are then re-sealed.

The gases thus produced are passed through a series of five wash-bottles containing successively water, bromine, a solution of soda, concentrated sulphuric acid, and absolute alcohol, and are then collected over water. The bromine retains the ethylene, the soda the bromine vapours, the sulphuric acid dries the gas, and, finally, the absolute alcohol dissolves eventually any formene which may be formed during the decomposition of barium ethylate, as suggested by M. Destrem (*Annales de Chemie et de Physique*, Series 5, vol. xxvii., p. 23). I may say at once that in my experiments no formene was produced. I found, on the contrary, that a small quantity of ethylene bromide is formed, and analysis of the gas collected over the water shows that it is composed only of hydrogen.

The contents of the sealed tubes are then introduced into a flask and distilled on an oil-bath to dryness. The residue is found to consist of acetate, carbonate of baryta, and unchanged barium ethylate.

The distillate is rectified by the Bel-Henninger method. The whole passes between 76° and 130°, the greater portion between 76° and 80°, and as the first fractions have the precise odour of acetic ether these were all united and boiled with a reflux condenser in the presence of caustic potash to saponify the ethers. The whole is further rectified a great number of times, and a small quantity of liquid separates, boiling at 115—117°, the temperature at which normal butylic acid boils, and which substance possesses the composition of this compound (C found to be 62·9 per cent, calculated 63·16 per cent; H found to be 16 per cent, calculated 15·79 per cent).

Finally, to identify this more certainly, 1 grm. was oxidised by means of chromic mixture, and an acid possessing the odour of butyric acid was obtained. We prepared the ammoniacal salt of this, then the amide, and proved that it melts at 114—115°, then that normal butyric amide melts at 115°. It has therefore been proved that normal butylic alcohol is formed by the action of ethylic alcohol on barium ethylate at 230—240°; but that the reaction is very slow, and only gives small yields. Using 500 grs. of the concentrated solution of barium ethylate I only obtained about 3 grs. of butylic alcohol. I remember that the syntheses of diamylic, dicœnanthylic, and dicaprylic alcohols were effected with excellent yields.

The reaction seems to be easier the higher the molecular weight of the alcohol employed.—*Comptes Rendus*, vol. cxxxiii., No. 5.

THE ASSAYING OF COMPLEX GOLD ORES.*

By ERNEST A. SMITH, Assoc.R.S.M., F.C.S.,
late Assistant Instructor in Assaying, Royal School of Mines, London.

(Continued from p. 90).

Cupriferous Ores.—Ores of this class are usually very troublesome to assay correctly by the fusion method, as they are generally poor in gold and silver, and frequently contain a large proportion of copper.

Owing to the readiness with which copper compounds are reduced during the fusion of the ore, some difficulty is experienced in passing the copper into the slag, and thus preventing the formation of cupriferous lead buttons. One part by weight of copper requires about sixteen parts of lead for cupellation, and though a smaller quantity of lead will pass the copper into the cupel, yet a sensible amount of gold and silver would in that case accompany the lead and copper, so that an incorrect result would be obtained (Percy). Under these circumstances it becomes necessary to add enough lead oxide to the charge not only to collect the gold and silver and oxidise the sulphur present, but to yield a button of lead sufficiently large to satisfactorily carry into the cupel all the copper present in the lead. With ores containing much copper this would give rise to the production of lead buttons inconveniently large for cupellation. Reliable results are obtained by direct fusion with ores containing from 20 to 30 per cent of copper, but when larger quantities are present, in most cases it is more satisfactory to remove it by a preliminary treatment with acid.

For this purpose the following method may be conveniently employed:—

From 30 to 50 grms, of the sample (according to the richness in gold and silver), are treated cautiously with fuming nitric acid until the ore is quite decomposed. The solution is warmed to expel all nitrous fumes, and diluted with water; a little hydrochloric acid or salt is then added to precipitate the silver. The solution is stirred well and allowed to settle until the liquid is clear. The supernatant liquid is removed by decantation, the liquid being poured off through a double filter-paper without disturbing the residue. After the liquid has been decanted as far as possible, the residue is transferred to the filter-paper by means of the wash-bottle. The filtrate, which should be bright and clear, contains the copper, and may be neglected. The residue containing the gold and silver is allowed to drain, and then dried, the filter paper burnt, and both added to the following mixture:—

Red-lead	30 grms.	
Charcoal powder	1·5	„
Sodium carbonate and borax, varying up to ..	30	„ together

The charge is fused in the ordinary way, the resulting button of lead cupelled, and the gold-silver bead parted in nitric acid.

When the quantity of residue is comparatively small it may be mixed with ten times its weight of granulated lead and scorified.

With a view to facilitate the settling of the finely divided precipitate of silver chloride the addition of a lead salt is sometimes recommended.

Preliminary treatment of cupriferous ores with acid, although requiring a greater expenditure of time than

* Abstract of Paper read before Institution of Mining and Metallurgy, May 15, 1901.

direct fusion methods, has the great advantage of producing lead buttons free from copper which may be cupelled direct. When treatment with nitric acid is not adopted, the ore may be assayed by fusion direct or by roasting previous to fusion. The following proportions arrived at experimentally by my father, the late Mr. Richard Smith, of the Royal School of Mines, London, may be taken for the direct fusion of the ore (Percy, "Metallurgy of Gold and Silver," Part I., articles on Assaying by R. Smith, p. 247). The quantity of ore is varied according to the richness in gold, and the percentage of copper present:—

Ore	10 to 50 grms.
Red-lead	200 to 300 ,,
Charcoal powder	1·5 to 3·5 ,,
Siliceous sand or glass ..	10 to 25 ,,

Charcoal powder is needed in charges for partially oxidised ores, but in the case of sulphide ores it may frequently be omitted, as the sulphur will reduce sufficient lead without it. The red-lead acts as the oxidising agent for the sulphur, but if a large quantity of sulphur is present a little nitre should be added to the above mixture to assist the oxidation. The fusion of the charge is effected in an earthen crucible at a comparatively low temperature. Cupriferous lead is liable to be obtained by this method from ores rich in copper, but when only moderate quantities of copper are present the results are satisfactory.

Hard cupriferous lead buttons should be scorified, with the addition of more lead if necessary, before being cupelled. It is very important that the scorification should be conducted at a low temperature, otherwise the lead is oxidised more rapidly than the copper and the object of the process defeated.

When the ore is roasted previous to fusion the quantity to be assayed, which may vary from 10 to 50 grms., should be weighed out before roasting. The oxidised product is then mixed with the following substances:—

Red-lead	100 grms.
Charcoal powder..	3·5 ,,
Sodium carbonate	20 to 30 ,,
Borax	15 to 30 ,,

The quantity of charcoal is varied according to the amount of iron oxide present, as indicated under Basic Ores. The fusion is conducted as before.

In the case of an auriferous antimonial copper ore the following proportions have been found suitable for making an assay by the fusion method of an ore containing about 30 per cent of copper:—

Ore..	30 grms.
Red-lead	150 ,,
Sodium carbonate	120 ,,
Nitre	18 ,,

The mixture is fused in the manner indicated under Antimonial Ores for charges containing nitre. The resulting lead button should be sufficiently free from antimony to be cupelled direct; no scoria should be formed on the surface of the cupel.

Ores with Galena and Zinc Blende.—Galena is completely reduced by metallic iron at a red heat with the formation of iron sulphide; consequently iron is the reducing agent generally employed in assaying gold ores containing galena. Ores containing only small proportions of galena may be roasted to effect the decomposition of the sulphide, but owing to the readiness with which lead sulphide volatilises when heated in the presence of sulphur dioxide, great care is needed in regulating the temperature to avoid loss of the precious metal.

If the quantity of galena in the ore is large, the amount of lead oxide added to the charge when fusing the ore may be lessened, or may entirely omitted if sufficient lead will be reduced without it. The fluxing and the fusion of the ore is conducted as described under the desulphurisation of pyritic ores with metallic iron.

Ores containing zinc blende should be roasted previous to fusion.

As this sulphide is practically infusible it tends to diminish the fusibility of other sulphides, such as stibnite and galena, when combined with them. If roasted with access of air zinc blende is decomposed, leaving the oxide which is infusible. Zinc blende is a substance difficult to roast absolutely sweet, although it has but little tendency to clot, and thus permits of a somewhat high temperature being employed in the earliest stages of the roasting. When the roasted product contains a large proportion of zinc oxide, difficulty is sometimes experienced in satisfactorily melting the charge. Zinc oxide combines with silica in definite proportions with the production of silicates difficult to fuse; but with borax and alkaline carbonate the oxide yields readily fusible compounds.

To facilitate the fusion of ores containing much zinc it is necessary to increase the proportion of borax and of sodium carbonate. In exceptional cases a little fluorspar may be added. Desulphurisation with metallic iron may also be employed for ores of this class, and this method is preferred by many assayers, as it occupies less time and obviates any loss of gold and silver which, if due care is not taken, may occur in the roasting operation with ores rich in blende owing to the volatile nature of zinc. In this method an ample supply of sodium carbonate should be used.

Telluride Ores.

Telluride gold ores have received considerable attention at the hands of assayers within recent years owing to the growing importance of this class of ores, and the difficulty of their assay as compared with ordinary ores. The presence of tellurium may be readily detected by the following simple method:—

A small quantity of the ore is heated in an open glass tube whereby a white sublimate of tellurous acid is formed. The portion of the tube containing the sublimate is removed by means of a file, and immersed in a small quantity of strong sulphuric acid in a test-tube. The presence of tellurium is indicated by the characteristic purple colour which it imparts to the acid when dissolved in the cold. The colouration produced by gently heating a small quantity of the ore with concentrated sulphuric acid is of little or no value, as the other minerals commonly associated with tellurium in gold-bearing ores interfere with or conceal this reaction.

A series of assays under varying conditions has been made by Charles H. Fulton (*Journ. Amer. Chem. Soc.*, 1898, xx., 586—597), who has arrived at the following conclusions, which are fully in accord with the author's experience with telluride ores.

For ores of this class scorification of any kind is bad, whether performed direct on the ore, or to reduce large or brittle buttons obtained from the fusion assay. The gold lost in the slag when the ore is scorified direct is very considerable, and there is also loss by volatilisation, the proportion increasing with the richness of the telluride. The crucible assay with direct cupellation is by far the best method, but special precautions are needed in conducting the assay. Telluride ores should on no account be roasted, as this causes considerable loss of gold and silver due to volatilisation.

A large excess of lead oxide is necessary to obtain good results; in the case of rich tellurides the quantity of ore should be decreased rather than the lead oxide increased, so that the lead button may not be too large to cupel directly (20 to 30 grms.). In the presence of lead oxide tellurium is readily converted into telluric acid, which combines with the lead oxide when the latter is in excess ($Te+4PbO=3Pb+PbO,TeO_3$), but if the contrary be the case the excess of telluric acid is volatilised and telluride of lead is produced. ($2Te+3PbO=TePb_3+TeO_3$).

Experience has shown that the loss of gold is very great if the charge for the fusion is not properly made up as regards the amount of lead oxide. The following charge may be conveniently employed for most telluride ores:—

Ore	50	grms.
Red-lead (according to the amount of tellurium present)	50 to 200	,,
Charcoal powder	1 to 2	,,
Sodium carbonate	50	,,
Borax	20	,,
Siliceous sand	10 to 30	,,

For very rich ores the following charge should be employed:—

Ore	10	grms.
Red-lead	100 to 150	,,
Charcoal powder	1	,,
Sodium carbonate	50	,,
Siliceous sand	5 to 10	,,

The sand is added to diminish the action of the lead oxide upon the earthen crucible. If the ore contain pyritic material, and the quantity of sulphur to be oxidised be large, the charcoal may be omitted, as sufficient lead will be reduced without it.

The whole of the constituents should be well mixed, then charged into the crucible, and covered with a thin layer of powdered salt. For the fusion of the charge the fire should be moderately hot, and the length of time in the furnace from forty to fifty minutes. Great care must be taken to avoid excessive heating at the commencement.

Since the loss of gold in the slag is much greater with telluride ores than in the case of ordinary ores, it is necessary in order to obtain accurate results that the slag should be powdered and re-melted with 30 grms. of red-lead, and 1·5 grms. of charcoal powder; the button of lead obtained being cupelled. The richer the ore, the more needful is it to clean the slag; in the case of ores very poor in tellurium it may sometimes be omitted. However, in the case of an ore with which the assayer is not familiar, it is better not to omit the examination of the slag until experience has shown that this may safely be done.

The cupellation of the lead is conducted at a low heat with litharge crystals just forming on the cupel. If the lead button is hard or brittle owing to the presence of base metals, and requires scorification previous to cupellation, this should be performed at a comparatively low temperature. When tellurium is present in the lead the gold button obtained from cupellation will be sub-divided into minute particles on the cupel. No difficulty is experienced in obtaining concordant results with telluride ores when due regard is given to the precautions indicated as to the proportion of lead oxide in the charge, and the regulation of the temperature for the fusion of the charge. Rapid fusion invariably gives low results.

(To be continued).

CONTRIBUTIONS TO THE SCIENCE OF THE NITROCELLULOSES.*

By G. LUNGE and J. BEBIE.

(Continued from p. 91).

C. *The Highest Degree of Nitration of Cellulose obtainable by means of Nitric-sulphuric Acid.*

On this question there are contradictory reports in print.

Eder obtained with a mixture of 3 parts concentrated sulphuric and 1 part fuming nitric acid a product which was found to contain from 13·74 to 13·91 per cent nitrogen after removing the lower nitration stages by washing with ether-alcohol, and he looks upon this as approximately pure cellulose hexanitrate (C_{12}...), *i.e.*, according to our nomenclature, dodecanitrate, which contains theoretically 14·14 per cent nitrogen.

Vieille and Vignon, under precisely similar conditions, obtained products with only 213—214 c.c. NO (13·4 per cent N), which would nearly correspond to an eleven-fold nitrated cellulose, and they consider this the highest attainable degree of nitration. But, according to Guttmann, this percentage of nitrogen might be exceeded, and he agrees with Eder's statement that it is possible to reach the dodecanitrate. Lunge and Weintraub, who worked with numerous proportions of concentrated sulphuric acid to fuming nitric acid, got no further than Vieille, viz., to the maximum of 214·4 c.c. NO. On the other hand, with nitric acid and phosphorus pentoxide, they obtained a product that closely approximated to hexanitrocellulose, with 13·87 per cent N.

The extension of the series of experiments described in the last section led to the following noteworthy results:—

TABLE XII.

Expt.	C.c. NO per 1 grm.	N per cent.	Increase.	Nitration mixture. H_2SO_4.	HNO_3.	H_2O.
1.	217·26	13·62	173	60·00	27·43	12·57
2.	219·28	13·75	174	62·10	25·79	12·11
3.	220·66	13·83	175	62·95	24·95	12·10
4.	219·34	13·75	175	63·72	25·31	10·97
5.	218·73	13·71	175	64·36	24·65	10·79

There were therefore now obtained products which approximated to the true hexanitrocellulose (14·14 per cent), more than all former bodies obtained directly from nitric sulphuric acid, viz., up to 13·83 per cent. But it is remarkable that this did not result from the most concentrated acid mixtures, but that those leading to the highest proportion of nitrogen contained relatively much water. Hence our experiments show, not only how higher stages of nitration than those already known can be attained, but also that these are produced by not quite concentrated acid mixtures, and consequently in a proportionately cheap manner.

The importance of this result demanded further research, which was instituted in the following manner:—A mixture of nitric acid 1·5 and sulphuric acid 1·82, in which the ratio of the two acids was the same as in the previous experiments, was diluted with varying quantities of water. The nitrations gave the following results:—

TABLE XIII.

Expt.	C.c. NO per 1 grm.	N per cent.	Increase.	Nitration mixture. H_2SO_4.	HNO_3.	H_2O.
1.	219·44	13·76	—	25·28	68·02	6·70
2.	218·95	13·72	173	64·55	26·55	8·88
3.	221·98	13·92	173	63·35	25·31	11·34

Hence, here also, with 11·34 per cent water, a proportion of N near to dodecanitrocellulose can be reached, viz., 221·98 c.c. NO = 13·92 per cent N. This is the highest nitration product of cellulose obtained by direct nitration without washing out the portion soluble in ether-alcohol, and which certainly consists principally of twelve-fold nitrated cellulose (C_{24}...).

After a few months, the percentage of nitrogen of a damp sample of this product had sunk to 13·5 per cent. This highest stage of nitration proved to be unstable. On repeating the experiment, we obtained again 13·6 to 13·8 per cent of nitrogen from the first analysis; but in later ones, and after keeping in a desiccator, 13·5 per cent was mostly obtained, and this proportion of nitrogen, corresponding to endecanitrocellulose, remained absolutely constant. This gives a further reason for adopting the formula C_{24}... instead of C_{12}....

It might be thought that the possibility, which we have demonstrated, of obtaining by direct nitration unusually highly nitrated celluloses has no practical value, as these products are not sufficiently stable; but, at least, we can conclude from our experiments that the highest practically obtainable degrees of nitration are not produced by the most concentrated acid mixtures, but by one containing a certain quantity of water.

* *Zeitschrift fur Angewandte Chemie*, 1901, Heft 20.

The ratio of sulphuric to nitric acid in the previous experiments was 2·50 to 2·52; the following experiments should show whether a change of this ratio within certain limits influences the favourable results obtained:—

1. Ratio of sulphuric acid to nitric acid = 3·3 : 1.

TABLE XIV.

Expt.	C.c. NO per 1 grm.	N per cent.	Increase.	Nitration mixture. H_2SO_4	HNO_3.	H_2O.
1.	215·70	13·53	176	75·33	22·80	1·87
2.	215·54	13·51	175	74·16	22·12	3·72
3.	216·50	13·57	—	72·97	21·63	5·40
4.	217·53	13·64	177	69·90	20·45	9·65
5.	217·10	13·61	176	68·31	20·49	11·20
6.	211·32	13·25	172	67·43	19·37	13·20

2. Ratio of sulphuric acid to nitric acid = nearly 2 : 1.

TABLE XV.

Expt.	C.c. NO per 1 grm.	N per cent.	Increase.	Nitration mixture. H_2SO_4	HNO_3	H_2O.
1.	217·35	13·62	176·5	67·32	32·53	0·15
2.	216·38	13·57	175	65·41	31·34	3·25
3.	217·50	13·63	176	63·75	30·80	5·45
4.	218·28	13·68	176	70·68	29·31	10·01

Thus, in this case also, rather higher nitration products were obtained with 10 to 11 per cent water than with the concentrated mixtures; it appears therefore, in the latter, that partial saponification of the ester takes place.

(To be continued).

THE ESTIMATION OF CARBONIC ACID IN WATER.*

By JOSEPH W. ELLMS and JAY C. BENEKER.

(Continued from p. 94).

Pettenkofer's and Trillich's Methods (continued).

IN spite of the above precautions, an error due to manipulation may arise on account of the extreme sensitiveness of barium hydroxide to atmospheric carbon dioxide. An average of twenty experiments made with the utmost caution, with boiled distilled water and barium hydroxide in well-ground glass-stoppered bottles, thoroughly vaselined, showed a loss of barium hydroxide equivalent to 1·5 parts per million of carbonic acid, with a range of from 1 to 3 parts per million.

Reinitzer (*Zeit. Angew. Chem.*, September 15, 1894) found in a solution of lime-water containing 1173·8 parts per million of calcium oxide, carbon dioxide equivalent to (*a*) 8·7 parts and (*b*) 9·3 parts respectively. The results were obtained by acidulation of the solution, expulsion of the carbon dioxide by heating, absorption and weighing of the gas in caustic potash. He states "we may assume the same conditions hold good with baryta-water."

The writers have found carbonic acid in calcium hydroxide solutions to range from 0 to 6 or 7 parts per million, although on an average the quantity was less than 3 parts per million. In the case of barium hydroxide solutions we have never found over 1 part per million of carbonic acid, and the average appears to be less than 0·5 part per million. The error arising, therefore, from dissolved carbonates in barium hydroxide solutions, in the absence of other salts which may effect their solution, we are inclined to believe, may be usually disregarded as a source of error.

The presence of suspended carbonates in the portion of the sample being titrated, however, is a source of error which must be carefully avoided. This arises from the direct solution of these salts in the titrating acid; and this is true whether oxalic acid is used or sulphuric acid, which latter was employed by the writers. This is shown by the following experiments:—

* *Journal of the American Chemical Society*, xxiii., No. 6.

Table showing Solubility of Suspended Carbonates by Titrating Acid.

I. Acid added to Alkali.

Solution used.	Containing no suspended carbonates. N/50 sulphuric acid.	Containing suspended carbonates. N/50 sulphuric acid.	Remarks.
C.c.	C.c.	C.c.	
10	3·9	5·0+	End-point indefinite with suspended carbonates.
Solution used.	N/20 (approx.) oxalic acid.	N/20 (approx.) oxalic acid.	
C.c.	C.c.	C.c.	
10	2·2	2·7+	End-point indefinite with suspended carbonates.

On another sample the following results were obtained:—

I. Acid added to Alkali.

Solution used.	Containing no suspended carbonates. N/50 sulphuric acid.	Containing suspended carbonates. N/50 sulphuric acid.	Remarks.
C.c.	C.c.	C.c.	
10	5·0	7·0+	End-point indefinite with suspended carbonates.

II. Alkali added to Acid.

10	5·0	7·0+	End-point indefinite with suspended carbonates.

It will thus be seen that the presence of suspended carbonates is quite inadmissible if accurate results are to be expected.

In both Pettenkofer's and Trillich's methods, the chief disturbing element is magnesium. Its salts must either be kept in solution as in Pettenkofer's method by the use of ammonium chloride, or allowed to precipitate out and be corrected for, as in Trillich's method. As the errors arising from the presence of magnesium salts are probably due to two different causes in the two methods, they will be discussed separately.

The erratic results often obtained with Pettenkofer's method are generally acknowledged. Tiemann ("Chem. Analyses des Wassers") admits that duplicate results may vary from 5 to 10 parts per million, and that the results are still more uncertain in the presence of magnesium salts. Thinking that ammonium chloride might be instrumental in holding carbonates in solution, some experiments were made to learn what effect it did have. The following experiments show the results obtained with a water which contained 59·2 parts per million of free and half-bound carbonic acid, but which contained no magnesium salts.

Table showing Effect of Ammonium Chloride in holding Carbonates in Solution.

No.	Solution (approx. N/20) barium hydroxide.	Saturated solution ammonium chloride.	Carbonic acid (CO_2) obtained.
	C.c.	C.c.	Parts per million.
1.	10	0	57·4
2.	45	0	60·0
3.	10	2	0·0 (*a*)
4.	20	2	0·0 (*b*)
5.	30	2	46·0
6.	45	2	56·6

(*a*) In the third experiment no loss of barium hydroxide resulted, and 38·4 parts per million of fixed carbonic acid were indicated in addition.

(*b*) No loss of barium resulted in the fourth experiment, and 1·9 parts per million of fixed carbonic acid were found in addition.

It will be noticed that as the concentration of the barium hydroxide solution increases, the ammonium chloride is less able to hold the carbonates in solution. Even with 45 c.c. of barium hydroxide solution, the amount is still less than with the same amount of alkali where no ammonium chloride is present. It is apparent from these experiments that carbonates may be held in solution where the concentration of the barium hydroxide solution is not great enough; and such a condition might easily arise in a water containing low amounts of magnesium but considerable carbonic acid, which latter would use up a large proportion of the barium hydroxide added.

In order to see whether ammonium chloride was able to hold in solution all of the magnesium which might be present, the following experiments were made:—

Table showing Effectiveness of Ammonium Chloride in holding Magnesium Salts in Solution.

Solution of Magnesium Sulphate. Total volume of Solution equal to 150 c.c.

Barium hydroxide solution (approx. N/20).	Saturated solution ammonium chloride.	Magnesium oxide added.	Magnesium oxide precipitated.
C.c.	C.c.	Parts per million.	Parts per million.
45	0·5	27	2·0
45	0·5	27	1·4
45	0·5	91	9·4
45	2·0	27	0
45	2·0	27	0
45	2·0	91	0
Solution of Magnesium Carbonate (total volume equal to 100 c.c.).			
45	2·0	15	0
45	2·0	15	0
45	2·0	15	0

It is evident that 0·5 c.c. of a saturated solution of ammonium chloride is not sufficient to hold in solution all the magnesium oxide that was added. Two c.c. are, however, able to hold in solution at least 90 parts per million of the oxide without any of it precipitating.

In Trillich's method the magnesium salts are allowed to precipitate as magnesium hydroxide, and are then corrected for as previously stated. It is quite evident, therefore, that unless the precipitation is complete an error is introduced into the correction. The following experiments show that this precipitation is not complete under certain conditions.

Table showing Incomplete Precipitation of Magnesium Hydroxide by Barium Hydroxide.

Solution of Magnesium Carbonate containing 15 parts per Million of Magnesium Oxide. Total volume of Solution equal to 100 c.c.

Barium hydroxide solution.	Magnesium oxide precipitated.	Magnesium oxide not precipitated.
C.c.	Parts per million.	Parts per million.
45	13·7	1·3
45	13·7	1·3
45	12·0	3·0
45	13·7	1·3
45	12·0	3·0
45	12·0	3·0
45	12·0	3·0
Average.. ..	12·6	2·4

From the above it will be seen that, on an average, 2·4 parts per million of magnesium oxide, equivalent to 2·6 parts per million of carbonic acid, were not precipitated in a solution containing 45 c.c. of an approximately 0·05 normal solution of barium hydroxide in a total volume of 100 c.c. From a large number of experiments made with a standard magnesium sulphate solution, it has been found that the same is true of this salt, *i.e.*, that the magnesium is but partially precipitated under certain conditions.

A large excess of barium hydroxide is necessary in order to effect practically complete precipitation, and unless this excess is maintained as the quantity of magnesium increases, the quantity of magnesium which remains unacted upon will also increase.

This is well shown by the following table, where constantly increasing amounts of magnesium were introduced into the solution.

Table showing Incomplete Precipitation of Magnesium Hydroxide with continually Increasing Amounts of Magnesium Sulphate.

Solution of Magnesium Sulphate. Total Volume of Solution equal to 100 c.c.

Barium hydroxide solution.	Magnesium oxide added.	Magnesium oxide precipitated.	Magnesium oxide not precipitated.
C.c.	Parts per million.	Parts per million.	Parts per million.
45	9·0	10	0
45	27·0	24	3·0
45	54·0	50	4·0
45	91·0	76	15·0

It will be noted that, in the first sample, slightly more than the amount of magnesium oxide actually present appears to be precipitated. This seems to be characteristic of results obtained on samples in which the magnesium is in small amount while the barium hydroxide is in large excess. It is due to the fact that the loss of barium hydroxide by carbonating is always greater in such cases.

The error from this cause, which may be called the "error of manipulation" and the error due to non-precipitation of magnesium hydroxide, act in opposite directions; the former tending to increase the apparent precipitation, and the latter to decrease it. It is probable, therefore, that the quantity of magnesium oxide not precipitated may be greater than is indicated above.

How seriously this error may affect results is shown by the following table. A standard solution was prepared and was found to contain, by Trillich's method, when no magnesium salts were present, 46·2 parts per million of free and half-bound carbonic acid. This result was the average of ten closely agreeing determinations on this solution; and the figures for the carbonic acid found, when magnesium was present, should be compared with it.

Table showing effect of Non-precipitation of Magnesium Hydroxide in Determinations of Carbonic Acid by Trillich's Method.

MgO added, equiv. to CO_2.	Ba_2OH_2 solution. N/20 (approx.).	CO_2 found by titration. Uncorr.	Theoretical correction for MgO.	CO_2 corrected for MgO.	MgO equiv. to parts per million CO_2. Precipitated.	MgO equiv. to parts per million CO_2. Not precipitated.
Parts per million.	C.c.	Parts per million.	Parts per million.	Parts per million.	Parts per million.	Parts per million.
10	10	49·5	10	39·5	3·3	6·7
10	10	50·6	10	40·6	4·4	5·6
10	10	49·4	10	39·4	3·2	6·8
10	10	49·4	10	39·4	3·2	6·8
10	10	49·4	10	39·4	3·2	6·8
20	15	59·2	20	39·2	13·0	7·0
20	15	57·9	20	37·9	11·7	8·3
20	15	57·9	20	37·9	11·7	8·3
20	15	57·9	20	37·9	11·7	8·3
20	15	57·9	20	37·9	11·7	8·3
30	15	64·6	30	34·6	18·4	11·6
30	15	63·4	30	33·4	17·2	12·8
30	15	64·6	30	34·6	18·4	11·6
50	20	83·0	50	33·0	36·8	13·2
50	20	81·6	50	31·6	35·4	14·6
50	20	83·0	50	33·0	36·8	13·2

Note.—Amount of magnesium oxide actually present is equal to 10/11 of amounts given as "MgO equivalent to parts per million of CO_2."

The results given above of course exaggerate the error because of the small amount of barium hydroxide and the

large amounts of magnesium. They serve to show, however, the error which might arise from this source.

The errors affecting the accuracy of Pettenkofer's and Trillich's methods may be briefly summed up as follows:—

1. The error due to the carbonating of the barium hydroxide as a result of manipulation. This is common to both methods, and tends to make results higher than they should be. With careful work it can be kept very low, and ought not to exceed 1 or 2 parts per million.

2. In Pettenkofer's method the solution of the carbonates by ammonium chloride, which tends to lower the results, seems to be the source of greatest error. The magnitude of this error appears to be governed by the concentration of the barium hydroxide solution and the amount of ammonium chloride present.

3. In the Trillich method the non-precipitation of the magnesium salts, as magnesium hydroxide, tends to lower the results. The excess of barium hydroxide over and above that necessary for the reaction, appears to be fully as necessary here as in Pettenkofer's method. It is probably best to have at least an excess of from 30 to 35 c.c. of 0·05 normal barium hydroxide solution for waters containing as much as 60 parts per million of magnesium oxide. The magnitude of this error may vary (even when the prescribed amount of 45 c.c. of an approximately 0·05 normal barium hydroxide solution is added to each 100 c.c. of water), from 2 to 5 parts per million. This amount may be exceeded with an insufficient excess of barium hydroxide.

Since the error due to unavoidable carbonating of the barium hydroxide in the course of manipulation increases the results, and all errors arising from solubility of carbonates or non-precipitation of magnesium hydroxide lowers them, these errors tend to neutralise each other. But if the error of manipulation is kept at a minimum, the lowering of the results due to other causes exceeds the increase, and in consequence too low results are obtained.

(To be continued).

ON THE METEORIC STONES WHICH FELL NEAR ZOMBA, BRITISH CENTRAL AFRICA, ON JANUARY 25TH, 1899. WITH NOTES ON THE CHEMICAL ANALYSIS OF SUCH BODIES.*

By L. FLETCHER, M.A., F.G.S.,
Keeper of Minerals in the British Museum.

(Concluded from p. 92).

Attracted Material: First Set of Extracts.

40. The Fe_2O_3,P_2O_5,SiO_2 0·4933 (§ 2) consists of Fe_2O_3 0·4895 (corresponding to Fe 0·3427), P_2O_5 0·0003 (corresponding to P 0·0001), (SiO_2 0·0028 due to the action on the vessels).

The phosphorus being present as Fe_2NiP (schreibersite) requires Fe 0·0004, Ni 0·0002.

The Ni(Co) due to nickel-iron (§ 2) is thus 0·0487 − 0·0002 or 0·0485.

Hence we have—

Extracted:—Nickel-iron	Fe	0·0342	0·3908
	Ni(Co) ..	0·0485	
Schreibersite			0·0007
Residue (§ 3)			0·3385
Total			0·7300
Weight taken			0·7421

No great stress can be laid on the loss of weight (0·0121), owing to the character of the necessary operations.

The percentage composition of the nickel-iron (0·3908) which has passed into solution is Fe 87·59, Ni(Co) 12·41.

Further, $3K_2SO_4.2CoSO_4$ 0·0166 corresponds to Co 0·0024; hence the percentage composition of the Ni(Co) is Ni 95·07, Co 4·93, and that of the nickel-iron is Fe 87·59, Ni 11·80, Co 0·61, Cu trace.

Attracted Material: Second Set of Extracts.

41. Fe_2O_3 0·0439 (§ 3) corresponds to Fe 0·0307; and the Ni(Co) is 0·0135.

Hence we have—

Extracted:—Nickel-iron	Fe	0·0307	0·0442
	Ni(Co) ..	0·0135	
Residue (§ 4)			0·2850
Total			0·3292
Weight taken			0·3366

As before, no stress can be laid on the loss of weight (0·0074); the percentage composition of the nickel-iron (0·0442) extracted in the second series of operations is Fe 69·46, Ni(Co) 30·54.

Attracted Material: Residue.

42. The Fe_2O_3,SiO_2 0·0450 (§ 4) consists of Fe_2O_3 0·0447 (corresponding to Fe 0·0306) and SiO_2 0·0013 (due to the action on the vessels).

$Mg_2P_2O_7$ 0·1137 corresponds to MgO 0·0412 (having regard to the smallness of this amount, the action of the nitric acid on the vessels must likewise have been small, and no deduction is made); the MgO being due to the silicates, other constituents in corresponding proportion must likewise be due thereto; hence the quantities will be (§ 35):—SiO_2 0·0420, MgO 0·0412, FeO 0·0245, MnO 0·0005, CaO 0·0011, making altogether 0·1093 of silicate decomposed by the hydrochloric acid; this leaves SiO_2 0·0027 (namely, 0·0447 − 0·0420) unallotted; the above quantities are only approximate, for the enstatitic and felspathic silicates are acted on by the acid and sodic solutions, and their proportions to the olivine are probably different from those which obtain in the unattracted material. Further, FeO 0·0245 of the silicate corresponds to Fe 0·0191, which is included in the above total Fe 0·0306; the Fe due to the alloy itself is thus 0·0115.

Hence we have—

Final residue (enstatite, &c.)	0·1409 (§ 4)
Silicate decomposed (olivine, &c.) ..	0·1093
Fe	0·0115
Ni(Co)	0·0072
Unallotted SiO_2	0·0027
Total	0·2716
Weight taken	0·2757

The loss in this case (0·0041) is, partly at least, oxygen; the amount of oxygen necessary to convert the whole of the iron into Fe_3O_4 would be 0·0044. That there is a certain amount of unoxidised metal present is shown by the effervescence of the material with the acid (§ 4); that there is oxide present is indicated by the extreme slowness of action of the mercuric solution on the material (§ 3). As there is only a small proportion of black opaque matter visible in the thin sections when examined with the microscope, and this is probably chromite, the oxidation had probably taken place during the analysis itself, as already suggested (§ 2). The iron and nickel in this residue corresponding to original metal will thus be Fe 0·0115, Ni(Co) 0·0072, corresponding to 0·0187 of alloy having the percentage composition Fe 61·50, Ni(Co) 38·50.

43. Hence we have the following results:—

	Nickel-iron.	Fe.	Ni(Co).	Percentage of Ni(Co).
First extracts ..	0·3908	0·3423	0·0485	12·41
Second extracts	0·0442	0·0307	0·0135	30·54
Residue	0·0187	0·0115	0·0072	38·50

* From the *Mineralogical Magazine*, vol. xiii., No. 59, 1901.

Hence, of the total nickel-iron contained in the attracted material, 86·13 per cent are removed in the first set of extractions, 9·75 in the second, and the remaining 4·12 is left partly as oxide and partly as metal, the latter protected from the mercuric solution by enclosing oxide or silicate. The variation of the percentage of nickel (cobalt) from 12·41 to 38·50, as the extraction proceeds, does not necessarily imply the existence of different alloys of nickel-iron in the material; it is probably a mere result of the easier oxidation of the iron than the nickel during exposure of the alloy to the atmosphere in the course of the operations.

Attracted Material: Mineral Composition.

44. Calculation, from these numbers, of the composition of the various residues leads to the following composition for the attracted material:—

	Grms.
Nickel-iron	1·2422
Olivine	0·3373
Enstatite	0·3474
Oligoclase	0·0875
	2·0144

for the proportion of the decomposed to the undecomposed silicate is known from § 42, and the proportion of the enstatite to the oligoclase may be taken to be the same as for the previous similar material (§ 28).

Mineral Composition of the Fragment.

45. From §§ 39, 44, the mineral composition of the complete fragment was—

	Grms.	Zomba. Percentages.	Linn County.* Percentages.
Nickel-iron	1·2422	8 61	10·54
Olivine	6·1267	42·44	41·85
Enstatite	5·0238	34·80	41·24
Oligoclase	1·2662	8·77	
Troilite	0·7005	4·85	6·37
Chromite	0·0758	0·53	—
	14·4352	100·00	100·00

Mineralogical Relationship to other Meteoric Stones.

The Zomba meteorite thus consists of a stony material composed of olivine and enstatite in nearly equal quantity admixed with a certain amount of oligoclase; embedded in this stony material are nickel-iron and troilite in considerable quantity and small amounts of chromite and schreibersite. In the aspect of the thin sections as seen under the microscope, in the proportions of the mineral constituents (§ 45), in the percentage composition of the silicate decomposed by hydrochloric acid (§ 36), and in that of the silicate obtained as a residue after the action of the acid and the sodic solution (§ 23), the Zomba meteorite closely resembles the stone which fell in Linn County, Iowa, U.S.A., on February 25th, 1847; different parts of one meteoric stone would generally show greater differences. The composition here assigned to the Zomba enstatite, after analysis of what is interpreted to be a mixture of enstatite and oligoclase, is very near to that found by Professor Tschermak for the coarse grains of enstatite which he was able to isolate from the Lodran stone for chemical determination (§ 27), and the specific gravity as calculated for the Zomba enstatite from the specific gravity of the mixture is virtually identical with the specific gravity directly determined by Professor Tschermak for the isolated Lodran Mineral (§ 29). Further, it is found that the "undecomposed residue," when itself subjected to the treatment used in the analysis of the unattracted material, loses nearly 12 per cent of its weight; the enstatite is chiefly acted upon by the acid, the oligoclase by the sodic solution (§ 30).

* *Monatsb. Ak. Wiss. Berlin*, 1870, p. 458.

THE PREPARATION OF OSMOTIC MEMBRANES BY ELECTROLYSIS.

By H. N. MORSE and D. W. HORN.

THE difficulties with which Pfeffer had to contend in the preparation of suitable semipermeable membranes for the investigation of osmotic pressure are well known, and need not therefore be rehearsed. Yet, notwithstanding the importance of the subject, no suggestion appears to have been made up to the present time which has helped to obviate any of those difficulties or in any degree to lessen them. The method of Pfeffer has not been improved, and, judging from the testimony of many who have tried it, attempts to prepare the Pfeffer cell usually fail to give satisfactory results.

In this connection, it occurred to the authors that if a solution of a copper salt and one of potassium ferrocyanide are separated by a porous wall which is filled with water, and a current is passed from an electrode in the former to another electrode in the latter solution, the copper and the ferrocyanogen ions must meet in the interior of the wall, and separate as copper ferrocyanide at all points of meeting, so that in the end there should be built up a continuous membrane well supported on either side by the material of the wall. The results of our experiments in this direction appear to have justified the expectation, and to be worthy of a brief preliminary notice.

The first problem concerned, of course, the effective removal of the air in the walls of the porous cups, since the presence of air obviously interferes with the formation of a sound membrane. For this purpose we have taken advantage of the strong "endosmose" which appears when a current is passed through a porous wall separating two portions of a dilute solution in which the electrodes are immersed. A boiled solution of potassium sulphate containing about 0·5 grm. of the salt in the litre was filled into the porous cup and into the beaker in which it was placed until the level of the liquid within and without reached nearly to the edge of the cup. On passing the current between the electrodes in the direction of the one within the cup, the liquid in the cup rises with a rapidity which increases with the dilution of the solution and with the intensity of the current. The water, in passing through the wall, appears to sweep out the air in an effective manner. As the liquid within the cup rose, it was removed from time to time with a pipette or by means of an intermittent syphon, and replaced by pouring more of the solution into the liquid outside the cup. The quantity of water forced through the wall in this way was considerable. As a rule, we have continued the electrolysis of the sulphate until 300 c.c. had been removed by the pipette or syphon, which required ordinarily about one hour. The cup was then emptied, washed, and placed in a large volume of distilled water until required for the deposition of the membrane.

To form the membrane, the wet cup was placed in a beaker and surrounded with an electrode of sheet copper, which completely encircled it. The other electrode—the one within the cup—was of platinum. After fixing the electrodes and connecting with the dynamo so that the current should begin to flow the instant the liquids touched the opposite walls of the cup, the copper solution (N/10 or N/5 sulphate), and that of the potassium ferrocyanide (also N/10 or N/5), were introduced as nearly simultaneously as possible. At first there is considerable endosmose in the direction of the current, *i.e.*, from the copper solution into that of the ferrocyanide, but no copper has ever been found to enter the cup, neither have any of the ferrocyanogen ions made their way into the copper solution. Both walls remained perfectly clean and free from discolorations except in a few instances, in which, for some reason not yet determined, metallic copper was deposited on the outside of the cup. At the upper edge of the cup, however, nearly midway between the two sides, there soon

appears a line of reddish-brown colour, showing in general the position of the membrane with respect to the outer and inner walls of the cup. The resistance usually rises quite rapidly, reaching in extreme cases 3000 ohms within an hour, while the endosmose diminishes correspondingly. The most rapid rise in resistance is observed in the less porous hard-burned cups. In the softer and more porous ones, the resistance may not exceed 200 or 300 ohms within an hour; and after a time, in such cases, the resistance begins to fall, owing apparently to the action of the accumulated alkali upon the membrane. If the solution of ferrocyanide in the cell is then replaced by a fresh one, the resistance begins to rise again.

Having obtained the desired resistance, the cell was removed, rinsed inside and out, filled with distilled water, and placed in a beaker containing water, care being taken, of course, not to allow any of the liquid from the inside to come in contact with the outer surface of the cup, and *vice versâ*.

Our first experiments were with ordinary porous battery cups holding approximately 250 c.c. On treating some of these in the manner described above until a resistance of from 1500 to 3000 ohms had been reached, they were tested as to the presence of a sound membrane within their walls by filling them one-third full of a normal solution of sugar, and then immersing them in water until the liquids within and without were on the same level. The water entered quite rapidly, and the cups usually began to overflow within from fifty to seventy-five hours. On breaking the cups, the membrane could be seen as a thin line along the fracture surfaces. Ordinarily it was located about midway between the two walls except where the material of the cup manifestly lacked uniformity. In such places the line would bend to one side or the other, and again return to its original direction beyond the uneven spots. The experiment was repeated with the same result with samples of all the various kinds of porous battery cups which had accumulated in the laboratory. It was found that a membrane which would at least exhibit osmotic activity could be made in the walls of any of them without difficulty. It was also tried with certain other cups which had been specially made with a view to the rapid filtration of liquids, and which were, therefore, much more porous than the ordinary battery cup. We could form a membrane in these, but it was necessary to exercise some care in the control of the current. Otherwise the resistance would occasionally drop in a marked degree, indicating a rupture of the membrane. The resistance, in the case of the cups last mentioned, could not be raised above a certain point, which was far below that which could easily be obtained in less porous cups.

With a view to testing the power of the electrolytically prepared membrane to resist pressure, we had made at a local pottery some bottle-shaped cells having a capacity of about 250 c.c. After depositing the membrane in these, in the manner described, they were filled with a normal solution of sugar, closed with rubber stoppers through which glass tubes had been passed, and placed in beakers of water standing upon the floor. Other lengths of tubing were added until the ceiling, 5·5 metres above the floor, was reached. Our tubes began to overflow in periods ranging from six to fifteen hours. When the open manometers were replaced by closed ones containing mercury, the cells failed; not, however, in consequence of ruptured membranes. In manufacturing such vessels, the bottom is made separately, and is inserted and cemented in its place after withdrawing the mould upon which the rest of the bottle is formed. The union between the two parts proved to be a weak one in the case of our cells. Before any considerable pressures were reached the bottoms gave way, permitting the sugar solutions to escape. In most instances the line of detachment could be seen, but not in all. We therefore added a little ferrocyanide to the solutions of sugar, and a little copper sulphate to the water in which the bottles stood in order to ascertain whether any of the sugar escaped at other places. A reddish-brown circular line then appeared where the two parts had been joined, but nowhere else.

Our next experiments were with small porous cups, such as are employed in making standard battery cells. These were about 85 by 25 m.m., internal measurement, and were provided with a flange at the top. We had found by previous experience that the forcing of a stopper into a cell is liable to injure the membrane, hence we cemented glass tubes in the cups before forming the membranes. In order to make the union more secure, channels were cut on the inside of the cups a little below the rim and parallel to it. The glass tubes, 125 m.m. long, and with external diameters somewhat less than the internal diameters of the cups, were provided with rubber rings at one end, of such thickness that rubber and glass together made moderately tight stoppers for the cups. These were pushed into the cups until the upper edges of the rubber rings were a little below the channels. The spaces above the rubber were then filled with the cement, which was made by mixing 5 parts of litharge with 1 part of glycerin. After hardening for forty-eight hours, the exposed surface of the cement was painted to protect it from liquids, with a solution of equal parts of rubber and paraffin in carbon bisulphide. The cups were then freed from air, and the membranes deposited in the usual manner. When the rubber stoppers carrying the closed manometers were inserted, provision was made for the escape of the superfluous sugar solution by manipulating a small steel rod between the rubber and the glass. The rod was afterwards extracted with a pair of forceps. In the first cell prepared in this way the pressure rose within an hour to 3·25 atmospheres, when the stopper began to give way. It was again crowded into place, and the pressure rose to a little over 3·5 atmospheres, but from this point the stopper was slowly pushed out of the tube. We then emptied the cell and shrunk the end of the glass tube in the flame to about three-fourths its original diameter, in order to give the stopper a more secure hold in the glass. With this modification we were able to secure pressures a little above 4·5 atmospheres. At that pressure, however, the sugar solution always began to ooze out between the manometer and the rubber stopper, and the stopper itself to move upward out of the tube.

We have found it impossible, with the crude manometer hitherto employed by us, to test our membranes at pressures much above 4·5 atmospheres; and it is clear that, to do this, rubber stoppers must be dispensed with, and some suitable metallic connection devised to join the manometer to the cell.

We have made no attempt as yet to measure osmotic pressure, our object at present being only to test the strength of the membranes. It seems improbable that the total osmotic pressure of concentrated solutions, *e.g*, molecular-normal ones, will ever be directly measured. It should, however, be practicable to construct cells in which the pressure of dilute solutions can be quite accurately determined. In that case, it should be feasible to measure the pressures of more concentrated ones by a differential method. For example, having obtained a membrane of such quality in a cell of such construction that the osmotic pressure of a tenth-normal solution can be satisfactorily measured, the pressure of a two-tenths normal solution could be determined by immersing the cell, not in water, but in a one-tenth normal solution, &c. It is probably safe to predict that if a method of determining molecular weights or electrolytic dissociation, by measuring osmotic pressure, is ever worked out, it will be developed along this line. That is, differences of pressure rather than the enormous totals will be measured. It is hoped that the electrolytic method of making semipermeable membranes, when developed by further study, may do away with what has hitherto appeared to be an insurmountable obstacle in the way of progress in this direction.—*American Chemical Journal*, xxvii., No. 1.

THE DISSOCIATING POWER OF DIFFERENT SOLVENTS.*

(A Summary).

By HARRY C. JONES.

(Continued from p. 96).

Inorganic Solvents (continued).

Sulphur Dioxide.—That liquid sulphur dioxide has the power to dissociate salts into their ions is shown by the work of Walden (*Ber. d. Chem. Ges.*, xxii., 2862), on the conductivity of solutions in this solvent. He worked with seven iodides, one bromide, and two sulphocyanates, and measured their conductivities at 0°, in dilutions ranging from a few litres to 100 or 200 litres. A few of his results are given:—

Potassium bromide.		Ammonium iodide.		Potassium sulphocyanate.	
v.	μv.	*v.*	μv.	*v.*	μv.
14·6	30·9	20·3	36·3	10·4	17·4
29·4	30·5	30·2	37·6	22·2	17·8
38·6	31·7	54·8	43·5	36·3	19·2
50·2	33·2	91·5	49·2	53·9	20·9
71·5	35·4			73·0	22·9

Walden compared these values with those of the corresponding salts in water at 0°, and found that the conductivities in liquid sulphur dioxide are from one-fourth to one-half the conductivities in water, under the same conditions.

He determined also the molecular weights of a number of salts in liquid sulphur dioxide, by the boiling-point method, and obtained the surprising result that many of the substances which conducted gave abnormally large molecular weights. Some results which are analogous to these were obtained by Franklin and Kraus (*Amer. Chem. Journ.*, xx., 848), in liquid ammonia as the solvent. The probable explanation is that while there is some dissociation into ions, there are also molecular aggregates present of a high degree of complexity. This would account for the facts observed.

Sulphur Dichloride, Sulphuryl Chloride, Thionyl Chloride, Phosphorus Oxychloride, Arsenic Trichloride, Antimony Trichloride.—Walden (*Zeit. Phys. Chem.*, xxv., 209), has quite recently studied the dissociating power of the above-named solvents, and finds that all of them break down electrolytes into their ions to a marked extent. An example or two will suffice:—

Tetraethylammonium iodide in phosphorus oxychloride.		Trimethylsulphine iodide in arsenic trichloride.	
v.	μv.	*v.*	μv.
250	28·91	250	51·44
500	33·45	500	57·90
750	26·11	750	60·75
1500	41·60	1500	66·60

Walden also studied solutions of salts in boron trichloride, phosphorus trichloride, phosphorus tribromide, antimony pentachloride, silicon tetrachloride, stannic chloride, sulphur trioxide, and bromine, and found that these substances have little or no ionising power. Phosphorus trichloride cannot dissociate electrolytes, while phosphorus oxychloride has a strong ionising power; similarly, antimony pentachloride cannot dissociate electrolytes, while the trichloride dissociates to a very considerable extent. We therefore cannot draw any conclusion in reference to the dissociating action of a solvent, knowing the dissociation in solvents which are closely allied to it chemically.

Organic Solvents.

Methyl Alcohol.—When we turn to the organic solvents, we find that considerable work has already been done on the conductivity of electrolytes dissolved in some of them. This is especially true of methyl and ethyl alcohols. Fitzpatrick (*Phil. Mag.*, xxiv., 378), studied the conductivities of calcium nitrate, lithium nitrate, lithium chloride, and calcium chloride in methyl alcohol, and found values which, though less than in water, were very considerable. Hartwig (*Wied. Ann.*, xxxiii., 58; xliii., 838), measured the conductivity of formic, acetic, and butyric acids in methyl alcohol. Paschkow (Charkow, 1892), studied the conductivities in methyl alcohol of potassium iodide, cadmium iodide, calcium nitrate, and potassium and sodium acetates. Völlmer (*Wied. Ann.*, lii., 328), worked out the conductivities of potassium and sodium iodides, potassium and sodium acetates, and lithium chloride in methyl alcohol, for a considerable range of dilution. Holland (*Wied. Ann.*, l., 263), studied the effect of non-electrolytes on the conductivity in methyl alcohol of potassium, sodium, calcium, lithium, and ammonium nitrates, and sodium chloride. Carrara (*Gazz. Chim. Ital.*, xxvi., [1], 119), carried out, by far, the most extensive investigation of salts in methyl alcohol which has yet been made. He measured the conductivities of the following substances at various dilutions:—Sodium chloride, iodide, methylate, acetate; lithium chloride, potassium chloride, bromide, iodide, methylate; ammonium chloride, bromide, iodide, and fluoride; tetraethylammonium chloride, bromide and iodide, tetramethylammonium iodide, triethylamine, diisopropylamine, and a number of sulphur derivatives. The conductivities in methyl alcohol of lithium and calcium chlorides, lithium, sodium, and barium bromides, potassium iodide, ammonium nitrate, and potassium acetate were determined by Kerler ("Dissertation, Erlangen," 1894), in Beckmann's laboratory. The conductivity of mercuric iodide in methyl alcohol was measured by Cattaneo (*Rend. R. Acc. Linc. Roma*, 1895); Schall (*Zeit. Phys. Chem.*, xiv., 701), determined the conductivity of hydrochloric, picric, oxalic, and dichloracetic acids in methyl alcohol; Kablukoff (*Zeit. Phys. Chem.*, iv., 429), also studied the conductivity of hydrochloric acid in methyl alcohol; and Kahlenberg and Lincoln (*Journ. Phys. Chem.*, iii., 26), measured the conductivities of ferric chloride and antimony trichloride in this solvent.

The most satisfactory work, on the whole, which has ever been done on the conductivity of solutions in methyl alcohol, is that of Zelinsky and Krapiwin (*Zeit. Phys. Chem.*, xxi., 35). Their work included a number of salts in pure methyl alcohol, as well as in a mixture of methyl alcohol and water, as we shall see later. They used in their work potassium bromide and iodide, ammonium bromide and iodide, cadmium iodide, tetramethylammonium bromide and iodide, tetraethylammonium iodide, a number of the substituted amines and sulphines, diethyl- and triethyl-stannic iodides, "fumaroid" dimethylsuccinic acid, oxalic acid, iodic acid, and trichloracetic acid.

A few of the results obtained by Zelinsky and Krapiwin are given below. These suffice to show the relation between the conductivities in methyl alcohol and in water. (See p. 95).

Potassium bromide.		Ammonium iodide.		Hydroxylamine hydrochloride.	
v.	μv.	*v.*	μv.	*v.*	μv.
32	69·02	16	72·24	16	54·39
64	76·70	32	78·74	32	62·18
128	83·60	64	85·0	64	69·52
256	88·96	128	91·14	128	75·98
512	93·26	256	96·20	256	81·21
1024	97·25	512	100·6	512	85·15
2048	100·1	1024	104·7	1024	87·30
4096	101·4			2048	85·70

Comparing these values of the molecular conductivity in methyl alcohol with those of potassium chloride at the same dilution in water, we see that they are not very different. The conductivity in methyl alcohol is about two-thirds to three-fourths that in water, under the same conditions.

* *American Chemical Journal*, xxv., No. 3.

An examination of the above results will show that even in as strong a dissociant as methyl alcohol, it is almost impossible to reach the value of μ_∞ directly by the conductivity method. That dilution at which the salt would be completely dissociated by this solvent is so great that it is impossible to apply the conductivity method to it with any degree of accuracy. It is therefore not possible to measure dissociation accurately, even in methyl alcohol, by the conductivity method.

Another method has been used by Jones (*Zeit. Phys. Chem.*, xxxi., 114), to measure the dissociation of salts by methyl alcohol. He so improved the boiling-point method that it can be used to measure dissociation in a solvent like methyl alcohol to a fair degree of accuracy. The salts used were potassium, sodium, and ammonium bromides; potassium, sodium, and ammonium iodides; potassium and sodium acetates; and calcium nitrate. The dissociation in methyl alcohol, as found by the boiling-point method, is, in round numbers, about two-thirds of that in water under the same conditions.

Ethyl Alcohol.—The number of those who have worked on solutions in ethyl alcohol is quite as large as in methyl alcohol. Fitzpatrick (*Phil. Mag.*, xxiv., 378), measured the conductivities of solutions of calcium chloride, calcium nitrate, lithium chloride, lithium nitrate, mercuric, magnesium, and ferric chlorides. Hartwig (*Wied. Ann.*, xxxiii., 58; xliii., 838), determined the conductivity of formic, acetic, and butyric acids in alcohol. Vicentini (*Biebl. Wied. Ann.*. ix., 131), used the following chlorides:—Ammonium, lithium, magnesium, calcium, cadmium, zinc, and cupric; while Cattaneo (*Biebl. Wied. Ann.*, xviii., 219, 365), studied mercuric, ferrous, and ferric chlorides, cadmium bromide, and cadmium iodide. Cattaneo found that these substances have a negative temperature coefficient of conductivity. Völlmer (*Wied. Ann.*, liii., 328), used a larger number of salts in ethyl alcohol than in water. These were potassium and sodium iodides, potassium and sodium acetates, sodium, lithium, and calcium chlorides, and calcium and silver nitrates. Kawalki (*Wied. Ann.*, liii., 324), compared the diffusion of a series of salts in water and in ethyl alcohol, and found that the rates of diffusion in the two solvents bore the same relation as the maximum molecular conductivities in these solvents. Reference should be made to the work of Paschkow ("Dissertation," Charkow, 1892), who measured the conductivities in ethyl alcohol of potassium and cadmium iodides, potassium and sodium acetates, and calcium nitrate; of Schall (*Zeit. Phys. Chem.*, xiv., 701), who worked with picric, oxalic, and dichloracetic acids; of Wildermann (*Zeit. Phys. Chem.*, xiv., 267), who studied the conductivities of di- and trichloracetic acids; of Kahlenberg and Lincoln (*Journ. Phys. Chem.*, iii., 26), whose work in ethyl alcohol included ferric chloride and antimony trichloride; and of Kablukoff (*Zeit. Phys. Chem.*, iv., 429), who measured the conductivity of hydrochloric acid in ethyl alcohol. The results obtained by Kahlenberg and Lincoln for the two chlorides with which they worked are given below:—

Ferric chloride.		Antimony trichloride.	
v.	μ_v.	v.	μ_v.
2·89	9·91	8·11	4·18
11·57	13·70	32·45	7·94
46·28	15·50	64·91	12·30
195·12	19·33	129·81	18·23
390·24	21·20	259·62	29·43

The dissociation of a number of salts in ethyl alcohol, as in methyl alcohol, has been measured by Jones (*Zeit. Phys. Chem.*, xxxi., 133), using the boiling-point method. These include potassium and sodium iodides, sodium and ammonium bromides, potassium and sodium acetates, and calcium nitrate. These salts were found to be dissociated by ethyl alcohol to from one-third to one-fourth the extent to which they are dissociated by water at the same dilution. It should be observed that dissociation as measured by the boiling-point method may not be directly comparable with dissociation as measured by the conductivity method, since the two sets of measurements are made at very different temperatures. It, however, seems very probable, from work which is now in progress in this laboratory, that the temperature coefficient of dissociation is quite small, in which case there should be only a small difference between the results obtained by the two methods.

Propyl and Allyl Alcohols; Isopropyl, Isobutyl, and Isoamyl Alcohols.—The dissociating power of alcohols higher in the series than ethyl alcohol has been determined for only a very few substances. A little work has, however, been done on the conductivity of a few electrolytes in the alcohols mentioned above. Schlamp (*Zeit. Phys. Chem.*, xiv., 272), measured the conductivity in propyl alcohol of solutions of lithium and calcium chloride, sodium iodide, and lithium salicylate, and compared the results with those obtained in ethyl alcohol and in water. The conductivity in propyl alcohol is somewhat less than 0·5 that in ethyl alcohol, under the same conditions of concentration and temperature. Carrara (*Gazz. Chim. Ital.*, xxvii., I., 221), made a few measurements of conductivity in propyl and amyl alcohols, and Hartwig (*Wied. Ann.*, xxxiii., 48; xliii., 838), determined the conductivity of formic, acetic, and butyric acids in amyl alcohol. The conductivity of triethylsulphine iodide in isopropyl alcohol was determined by Carrara (*Gazz. Chim. Ital.*, xxvii., I., 221).

Two substances have been studied in isobutyl alcohol; hydrochloric acid by Kablukoff (*Zeit. Phys. Chem.*, iv., 432), and picric acid by Schall (*Zeit. Phys. Chim.*, xiv., 707). Their results are given below:—

Hydrochloric acid in isobutyl alcohol.		Picric acid in isobutyl alcohol.	
v.	μ_v.	v.	μ_v.
0·49	2·15	101·6	1·48
2·56	3·08	307·4	1·91
50·33	3·84	511·0	2·20
136·62	3·99	638·0	2·30

Kablukoff (*Zeit. Phys. Chem.*, iv., 429), also worked with solutions of hydrochloric acid in isoamyl alcohol, and obtained the following results:—

Hydrochloric acid in isoamyl alcohol.	
v.	μ_v.
3·42	1·79
5·44	1·66
8·93	1·47
14·29	1·42
25·42	1·25

The above results bring out the remarkable fact that the molecular conductivity of hydrochloric acid in isoamyl alcohol decreases with increase in dilution. This is the first time we have encountered such a relation.

Ether.—Very little has thus far been done on the conductivity of ethereal solutions. Cattaneo (*Atti. R. Acc. delle Scienze, Torino*, xxviii., 329; *Rendic. R. Acc. dei Lincei*, [5], ii., 1; sem., 295), has measured the conductivity of ethereal solutions of cadmium iodide, cadmium bromide, ferrous and ferric chlorides, aluminium, mercurous and stannous chlorides, salicylic acid, and hydrochloric acid. The conductivities were determined at temperatures ranging from 10° to 30°, and it was found that the conductivity decreased with rise in temperature—ethereal solutions have a negative temperature coefficient of conductivity. Cattaneo also found that the molecular conductivity of hydrochloric acid in ether decreased with increase in dilution. This is analogous to the results obtained by Kablukoff, who found a similar result for

hydrochloric acid in isoamyl alcohol. Indeed, Kablukoff (*Zeit. Phys. Chem.*, iv., 431), found also that the conductivity of hydrochloric acid in ether decreased with the dilution.

Acetone and other Ketones.—The conductivities of a number of salts of the alkalis in acetone were published by Cattaneo (*Rend. R. Acc. dei Lincei*, [5], 40, 2e sem., 63—75), some five years ago. About the same time a paper appeared by St. v. Laszczynski (*Zeit. Elek. Chem.*, 1895, 55), on the conductivity of solutions of some salts in acetone. A number of salts were included :—Lithium and mercuric chlorides, potassium iodide, silver nitrate, and potassium, sodium, and ammonium sulphocyanates. The conductivity of solutions in acetone has also been measured by Carrara (*Gazz. Chim. Ital.*, xxvii., I., 207); but the following results are taken from the work of von Laszczynski.

Lithium chloride.		Potassium sulphocyanate.		Silver nitrate.	
v.	μ_v.	*v.*	μ_v.	*v.*	μ_v.
12·44	4·58	2·04	24·4	143·9	13·3
24·88	6·61	4·08	34·5	287·8	14·7
49·76	9·40	8·16	44·2	575·6	16·5
99·52	12·9	16·32	55·1		
		32·64	66·6		

Kahlenberg and Lincoln (*Journ. Phys. Chem.*, iii., 27), measured the conductivity of solutions of ferric, cupric, and stannous chlorides, and antimony trichloride, in acetone; and Dutoit and Aston (*Comptes Rendus*, cxxv., 240), as well as Dutoit and Friderich (*Bull. Soc. Chim.*, [3], xix., 321), studied a number of solutions in acetone and other ketones. Dutoit and Aston pointed out that those solvents which dissociate to the greatest extent are polymerised, as is shown by the surface-tension method of Ramsay and Shields (*Zeit. Phys. Chem.*, xii., 433). They raise the question as to whether there is not a necessary relation between the polymerisation of the solvent and its dissociating power. To test this they measured the conductivity of salts in a number of solvents. In acetone they used cadmium iodide and sodium salicylate.

In addition to acetone they worked with methylethylketone and methylpropylketone. In the former solvents they used mercuric chloride, cadmium iodide, ammonium sulphocyanate, and sodium salicylate; in the latter, cadmium iodide, ammonium sulphocyanate, and sodium salicylate. They found larger conductivity in the methylethyl- than in the methylpropylketone, but the conductivity in acetone was greater than in methylethylketone. The following data will illustrate these statements :—

	Acetone.	Methylethyl-ketone.	Methylpropyl-ketone.
	μ_v.	μ_v.	μ_v.
CdI_2 ($v=64$) ..	11·6	5·58	2·13
,, ($v=128$) ..	11·9	5·48	1·55

Dutoit and Aston conclude from their work, together with that of Kablukoff (*Zeit. Phys. Chem.*, xii., 433), that there is a general relation between the polymerisation of the molecules of a solvent and its dissociating power.

The work of Dutoit and Friderich (*Bull. Soc. Chim.*, [3], xix., 321), confirms that of Dutoit and Aston. They find that the values of μ_m for any electrolyte in different solvents, is a direct function of the amount of polymerisation of the molecules of the solvent, and inversely as the coefficients of viscosity of the solvents.

In connection with their work in acetone as the solvent they make this remarkable statement (*Bull. Soc. Chim.*, 334) :—"We have found by the boiling-point method that the following salts in acetone have normal molecular weights : Cadmium iodide, lithium chloride, sodium iodide, mercuric chloride, and ammonium sulphocyanate," and these substances in acetone conduct the current. Some results already obtained in this laboratory seem to throw light on this apparent discrepancy.

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 6, August 5, 1901.

New Method of Preparation of Aniline and the Analogous Alkalis.—Paul Sabatier and J. B. Senderens.—In several previous researches the authors have shown that free hydrogen, acting at low temperatures in presence of certain finely divided metals, is able to fix itself directly on to various unsaturated organic molecules. This is a general method, which can be applied with advantage to the usual methods for hydrogenation performed by nascent hydrogen (from hydriodic acid in sealed tubes, sodium amalgam and water, iron, zinc or tin, and dilute acids). It is the recently prepared nickel, from reduction of its oxide, that the greatest activity has been found. Reduced cobalt, iron, copper, or platinum in a finely divided state possess analogous powers. The authors find that their method of hydrogenation allows of the transformation of nitrobenzene or analogous nitrated derivatives into aniline or corresponding alkalis.

Vapour-tension of Solutions. Arrhenius's Hypothesis.—A. Ponsot.—Unsuitable for abstraction.

MISCELLANEOUS.

Birkbeck Institution.—A competition for twenty Ravenscroft Entrance Studentships of Two and a-half Guineas each will be held on Tuesday and Wednesday September 17 and 18. These Studentships are open to intending Students, and to Students of the Institution of not more than one year's standing. All Candidates must be between the age of 16 and 25. Names must be given in on or before September 10.

The Chemical Laboratory at Wiesbaden.—During the Summer Term, 1901, the Chemical Laboratory Fresenius was attended by forty-four Students. Of these, thirty-one were from Germany, two from England, two from Austria, two from Russia, one from Luxemburg, one from Belgium, one from Holland, one from Italy, one from Norway, one from the United States of America, and one from Rhodesia in South Africa. There were three Assistants in the Instruction-Laboratory, and twenty-four in the Versuchsstationen (private laboratories). In the certified staff of teachers there has been no change. To this staff belong the Directors, Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, Prof. Dr. E. Hintz, and also Dr. Med. G. Frank, Dr. W. Lenz, Dr. L. Grünhut, and J. Huber (Architect). The next Winter Term begins on October 15. During the Summer Term, 1901, besides the scientific researches, a great number of analyses were undertaken in the different departments of the Laboratory (Versuchsstationen), on behalf of trade, manufacture, mining, agriculture, and hygiene.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Estimation of Phosphorus by Colour in Basic Steel.—Can any reader give me details of process, or give references as to where details may be found ?—Phos.

BENZOL 90 %

Wanted in large quantities, supplied yearly.
Address, "F. N. V. 1462," care of
Rudolf Mosse, Frankfort-on-Maine.

THE CHEMICAL NEWS.

Vol. LXXXIV., No. 2180.

(STUDENTS' NUMBER).

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

Candidates for any Degree in this University must have passed the Matriculation Examination. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, and Medals depending upon them, are open to Women upon exactly the same conditions as to Men.

There are two Examinations for Matriculation in each year; one commencing on the second Monday in January, and the other on the second Monday in June.

The Examination is conducted by means of Printed Papers; but the Examiners are not precluded from putting, for the purpose of ascertaining the competence of the candidates to pass, *viva voce* questions to any candidate in the subjects in which they are appointed to examine. These Examinations may be held not only at the University of London, but also, under special arrangement, in other parts of the United Kingdom, or in the Colonies.

Every candidate for the Matriculation Examination must, not less than five weeks before the commencement of the Examination, apply to the Principal for a Form of Entry, which must be returned not less than four weeks before the commencement of the Examination, accompanied by a Certificate showing that the candidate has completed his sixteenth year, and by his Fee for the Examination. As no candidate can be admitted after the List is closed, any candidate who may not have received a Form of Entry within a week after applying for it must communicate immediately with the Principal, stating the exact date of his application and the place where it was posted.

Every candidate entering for the Matriculation Examination for the first time must pay a Fee of £2 to the Principal. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him, but he shall be allowed to enter for any subsequent Matriculation Examination upon payment, at every such entry, of an additional Fee of £1, provided that he comply with the Regulations in the preceding paragraph.

Candidates are not approved by the Examiners unless they have shown a competent knowledge in each of the following subjects:—Latin (two papers); English (two papers). Any one of the following Languages or Sciences:—Greek, French, German, Sanskrit, or Arabic; Mathematics (two papers); General Elementary Science (two papers); Elementary Mechanics, Chemistry, Sound, Heat and Light, Magnetism and Electricity, Botany.

A Pass Certificate, signed by the Principal, will be delivered to each successful candidate after the Report of the Examiners has been approved by the Senate.

The first six candidates in the Honours Division of not more than twenty years of age at the commencement of the Examination will respectively receive an Exhibition or a Prize as follows:—The first of such candidates will receive an Exhibition of £30 per annum for the next two years. The second will receive an Exhibition of £20 per annum for the next two years. The third will receive an Exhibition of £15 per annum for the next two years; such exhibitions are payable in quarterly instalments provided that on receiving each instalment the Exhibitioner declares his intention of presenting himself either at the two Examinations for B.A., or at the two Examinations for B.Sc., or at the Intermediate Examination in Laws, or at the Preliminary Scientific and Intermediate Examinations in Medicine, within three academical years from the time of his passing the Matriculation Examination. The fourth will receive a prize to the value of £10 in books, philosophical instruments, or money; and the fifth and sixth will each receive a prize to the value of £5 in books, philosophical instruments, or money.

Any candidate who may obtain a place in the Honours Division at the Matriculation Examination in January is admissible to the Intermediate Examination either in Arts or in Science in the following July.

Intermediate Examination in Science.

The Intermediate Examination in Science will commence on the second Monday in July.

No candidate (with the exception of such as have obtained Honours at the Matriculation Examination in the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. This Examination will consist of two printed papers and a practical examination.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.Sc. Examination.

The B.Sc. Examination will be held on the fourth Monday in October.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously.

The Fee for this Examination is £5.

Examination for Honours.

For the examination for Honours in Chemistry two papers will be set and a practical examination.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

Doctor of Science.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

Every candidate for this Degree must state in writing the special subject within the purview of the Faculty of Science, as set out in the Programme of the B.Sc. Examination, upon a knowledge of which he rests his qualification for the Doctorate; and with the Form of Entry he shall transmit an original Dissertation or Thesis (at least six copies), printed, type-written, or published in his own name, treating scientifically some special portion of the subject so stated, embodying the result of independent research, or showing evidence of his own work, whether conducted independently or under advice, and whether based on the discovery of new facts observed by himself, or of new relations of facts observed by others, or, generally, tending to the advancement of Science. Every candidate may further specify any printed contribution or contributions to the advancement of Science which he has at any time previously published. If the Dissertation or Thesis be approved by the Examiners, the candidate shall be required to present himself at the University upon such day or days within the first twenty-one days of June as may be notified to him, and shall, at the discretion of the Examiners, be further tested, either orally or practically, or by printed questions or by all of these methods, with reference both to the special subject selected by him and to the Thesis.

Preliminary Scientific (M.B.) Examination.

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the second Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

The Fee for this examination is Five Pounds.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry—W. Odling, M.A., F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years. Students of Chemistry can obtain the degree of B.A. by passing preliminary examinations in Arts and in Science, and a final Honour examination in Chemistry. Chemistry may also be taken as part of the examination for a Pass degree. Graduates of other Universities suitably qualified can obtain the degree of Bachelor of Science after an approved course of study or research and two years' residence.

University Laboratory.—Demonstrators, W. W. Fisher, V. H. Veley, F.R.S., J. E. Marsh.—The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

Christ Church Laboratory.—A. Vernon Harcourt, F.R.S.

Balliol College Laboratory.—D. H. Nagel, H. B. Hartley.

Magdalen College Laboratory.—D. R. Wilson, J. J. Manley.

Queen's College Laboratory.—G. B. Cronshaw, A. F. Walden.

Scholarships of about the value of £80 are obtainable at the majority of the colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the Examination Statutes; the Student's Handbook to the University; and from the professors and college tutors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry—G. D. Liveing, M.A., F.R.S.

Jacksonian Professor of Natural and Experimental Philosophy—J. Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in any term of residence or before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

A graduate of another University may be admitted as an "advanced" student, and obtain a degree after two years' residence in the University.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science in King's, Trinity, St. John's, St. Peter's, Clare, Trinity Hall, Queen's, Jesus, Christ's, Emmanuel, Sidney, Pembroke, Caius, and Downing Colleges; the dates of the examinations vary, but are always fully advertised.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instructions. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, or from the *Cambridge University Calendar.*

UNIVERSITY OF DUBLIN.

Trinity College.

Professor of Chemistry—J. Emerson Reynolds, D.Sc., M.D., F.R.S.

Assistant Lecturer—Emil A. Werner, F.C.S., F.I.C.

Demonstrators—W. Haughton, M.B., and W. C. Ramsden.

The general Laboratories include working accommodation for 120 Students, and the Quantitative and Research Laboratories for about 40 Students. The Laboratories will open on the 2nd of October. Lectures will commence about November 1st.

The Laboratories and the Lectures ofthe Professor of Chemistry can now be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The following Lectures are delivered:—

1. *Inorganic Chemistry and Chemical Philosophy.*—Elementary, first year; Advanced, including Physical Chemistry, second year.
2. *Organic Chemistry.*—General, second year; advanced, third year.
3. *Metallurgy.*—A Course for Engineering and Technical Students.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The Summer Course of Practical Chemistry for Medical Students begins during the first week in April and terminates with the first week in July.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

By recent decrees, Prizes in Chemistry and Physics will be given in future at the October (Arts) Entrance Examination, and also at the Terminal Examinations of the Junior and Senior Freshmen Years.

Similarly, two Science Scholarships will be obtainable by Freshmen, and tenable for five years. These Foundation Scholarships are paid £20 per annum, have free commons, and their chambers and tutorial fees are at half the usual rates.

KING'S COLLEGE.

(Division of Engineering, Architecture, and Applied Science).

Professor of Chemistry—J. M. Thomson, F.R.S., F.C.S.

Lecturer—Herbert Jackson, F.C.S.

Demonstrator—P. H. Kirkaldy, F.C.S.

The Academical Year consists of Three terms. The days fixed for the Admission of New Students in the Academical Year 1901-1902 are October 3, January 16, and April 24.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a view of the conditions suitable for the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic Elements and their principal compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated. Examinations of the Class, both *vivâ voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, and they go through a course of Chemical Analysis, both by liquid tests and the blowpipe, analysis of ores, liquids, &c., and Elementary Volumetric Analysis.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students

who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Special hours and fees are arranged for the convenience of such Third Year Students as wish to study Analytical Chemistry.

Fees.—Chemistry per term, £3 3s.; per ann., £8 8s.; Practical Chemistry per term, £4 4s.; per ann., £10 10s.; Experimental and Analytical Chemistry—Five days a week: One month, £4 4s.; Three months, £10 10s.; Six months, £18 18s.; Nine months, £26 5s. Three days a week: One month, £2 12s. 6d.; Three mos., £6 6s.; Six mos., £11 11s.; Nine mos., £15 15s.

METALLURGY.

Professor—A. K. Huntington, F.I.C., F.C.S., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is paid to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery.

PHOTOGRAPHY.

Lecturer—Prof. J. M. Thomson, F.R.S., F.C.S.

In addition to the regular College Course in Photography occasional classes may be formed. For further particulars application should be made to Prof. Thomson.

EVENING CLASSES.

Classes for Evening Instruction in various subjects are held during the Winter Session.

UNIVERSITY COLLEGE.

FACULTY OF SCIENCE.

Professor—William Ramsay, LL.D., F.R.S., &c.

Assistants—Morris Travers, D.Sc.; E. C. C. Baly, F.I.C.; and F. G. Donnan, M.A., Ph.D.

The Session is divided into three Terms, as follows:—First Term, from Wednesday, October 2nd, till Friday, December 20th; Second Term, from Tuesday, January 14th, till Wednesday, March 26th; Third Term, from Tuesday, April 22nd, till Saturday, June 14th. Class Examinations begin on June 16th.

Junior Courses of Inorganic Chemistry.

First Term: Tuesday, Thursday, and Saturday at 10., Latter half of Second and Third Term: Tuesday, Thursday, and Saturday. Fee:—£4 4s.

These Courses will each consist of about thirty lessons, partly theoretical and partly practical, on the non-metallic elements. Frequent exercises will be given.

Senior Course of Inorganic Chemistry.

First and Second Terms: The Class meets four times a week, on Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

Fees:—For the Course, £7 7s.; Perpetual, £9 9s.; for the First or Second Terms, £4 4s.

This Course and the Practical Class cover the subject as prescribed for the Preliminary Scientific (M.B.) and Int. Examination in Science of the University of London.

For the Preliminary Scientific Examination Students who take the three subjects for that examination in July attend during the First and Second Terms.

Advanced Course of Chemistry.

Second and Third Terms.—The class meets twice a week, on Tuesdays and Thursdays, at 9, beginning in January. The hour will be altered by special arrangement with the class if necessary.

Fee:—For the Course, £3 3s.; for a Term, £2 2s.

This Course will be found suitable for those about to proceed to graduation as Bachelor of Science in London University, and to those who intend to choose Chemistry as a profession. Such students should also work in the Laboratory during as many hours as they can spare.

Organic Chemistry.

Mondays and Wednesdays, at 9, during the session.

This Course of Organic Chemistry is intended for those who are studying the subject from a scientific standpoint. Candidates for Honours at the Int.M.B. are, however, recommended to attend this Course instead of the Special Summer Course.

The Course includes the subjects required at the B.Sc. Examination, Pass and Honours; but no previous acquaintance with Organic Chemistry will be expected of those joining the Class.

Fee:—For the Course, £6 6s.; for a Term, £2 12s. 6d.; for a Second Course, £3 3s.

Practical Classes.

Practical Classes in Inorganic and Organic Chemistry are conducted by the Assistants.

Analytical and Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

The Laboratory Course includes the Practical Chemistry required at the following Examinations of the University of London:—Prel. Sci. (M.B.), Intermediate M.B., Intermediate Science, B.Sc.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Course qualifies Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. The Tuffnell Scholarship (about £80 for two years) will also be competed for in the Session 1901-1902; also the Clothworker's Scholarship of £30.

ROYAL COLLEGE OF SCIENCE AND ROYAL SCHOOL OF MINES.

Professor—W. A. Tilden, D.Sc., F.R.S.

Assistant Professor—W. P. Wynne, D.Sc., F.R.S.

Demonstrators—H. Chapman Jones and M. O. Forster, Ph.D., B.Sc.

Assistants—G. S. Newth, G. T. Morgan, D.Sc., and J. C. Philip, M.A., Ph.D., B.Sc.

The Royal College of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Science and Art Department. The Royal School of Mines is incorporated with the Royal College of Science. Students entering for the Associateship of the Royal School of Mines obtain their general scientific training in the Royal College of Science. The instruction in the Royal College of Science is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of

study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Royal College of Science, or of the Royal School of Mines. Students who are not candidates for the Associateship are permitted to enter as occasional students in one or more special branches of science, and on passing the examination receive a Certificate to that effect. The Associateship of the Royal College of Science is given in one or more of the following divisions :—Mechanics, Physics, Chemistry, Biology, and Geology, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction, which lasts for three years, is the same for all the divisions during the first year, after which it is specialised in accordance with the Scheme detailed in the Prospectus of the School.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third year, the successful candidates being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first year, and, in the second and third year, those subjects prescribed as necessary for the division in which he seeks to obtain his Associateship. A student who goes through the prescribed course of instruction in any subject and passes the necessary examinations receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table :—

	Lectures.	Laboratory.
	£	£
Chemistry	3	13
Physics	5	12
Biology with Botany	5	12
Geology with Mineralogy ..	4	8
Mechanics	4	6
Metallurgy	2	13
Mining	4	
Astronomical Physics	2	3
Mine Surveying	10	

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to £40.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

Summer Courses for Teachers.—Short courses of instruction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 250 teachers are admitted to them, and they receive third class railway fare to and from South Kensington, and a sum not exceeding £3 towards their expenses. (See Science and Art Directory).

Working Men's Lectures.—Notification of these will be given in the newspapers.

THE SCHOOL OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Sixtieth Session will commence on Tuesday, October 1st, 1901.

Professors—Chemistry, J. Norman Collie, Ph.D., F.R.S., F.I.C.; Botany, J. Reynolds Green, Sc.D., F.R.S., F.L.S. (Dean); Pharmaceutics, Henry G. Greenish, F.I.C., F.L.S.

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the end of March. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies.

Prospectuses and further information may be obtained from Mr. Richard Bremridge, Secretary and Registrar, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

UNIVERSITY OF WALES.

Professor—J. J. Sudborough, D.Sc. (Lond.), Ph.D. (Heidelberg), F.I.C.

Demonstrators—H. Hibbert, M.Sc. (Vic.)., and A. Brooke, Ph.D. (Strassburg).

Lecturer in Agricultural Chemistry—J. Alan Murray, B.Sc. (Edin.).

The College is open to male and female students above the age of sixteen years. The Session commences on Tuesday, October 1, on which day all Students will be expected to meet the Professors in the Examination Hall of the College.

Lecture Courses.—(1) Matriculation Course; two lectures weekly throughout the Session. (2) Intermediate Science Course; four lectures weekly throughout the Session. (3 and 4) B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, three lectures weekly on General and Physical Chemistry. (Courses A and B will generally be given in alternate Sessions; for 1901-1902, Course A). (5 and 6) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly during the Michaelmas and Lent terms.

Laboratory Courses.—The Laboratory is open daily from 10 a.m. to 1 p.m., and from 2.15 to 5 p.m., except on Wednesdays and Saturdays. Classes for the Systematic Study of Qualitative and Quantitative Analysis will be formed, and Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the University of Edinburgh and the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spentat Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 12s. 6d. per term, and for twelve hours, 25s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 18, and

exhibitions are awarded at the end of the Session on the results of the class examinations.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Prospectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

A CONSTITUENT COLLEGE OF THE UNIVERSITY OF WALES.

Chemistry.—Professor, James J. Dobbie, M.A., D.Sc. Demonstrator, Alexander Lauder, B.Sc., F.C.S. Assistant Lecturer in Agricultural Chemistry (vacant). Scholar Assistant, Godfrey Rotter.

Physics.—Professor, E. Taylor Jones, D.Sc.

The Session opens October 1st, 1901. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Matriculation Course.—Subjects: Those prescribed for the Matriculation Examination of the University of Wales. Fee for the Session £3 3s.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Session, £3 13s. 6d.

B.Sc. Course.—Inorganic and Physical Chemistry. Fee for the Session, £3 3s.

Agricultural Chemistry.—Fee, £2 2s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 4 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s.; twenty-four hours, £4 4s. Composition Fee for all Laboratory Classes of the Intermediate Science Course taken in one year, £4 4s.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and students can make one *Annus medicus* at the college. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

Professor—C. M. Thompson, M.A., D.Sc., F.C.S.

Demonstrators—E. P. Perman, D.Sc., F.C.S., and A. A. Read, F.I.C., F.C.S.

The Session commences October 7th, and terminates on June 27th, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 50 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of about 80 lectures held during the Lent and Summer terms in continuation of the Junior Course, and is the qualifying course for the Intermediate Examination of the University of Wales. Together with laboratory practice, it will cover the subjects required for the Intermediate Examination in Science and the Prel. Sci. (M.B.) Examination of the University of London. Fee, £4 4s.

The Senior Course consists of some 90 lectures on Organic Chemistry; Fee, £3 3s.

A course of 20 lectures on Qualitative Analysis and a short course on Organic Chemistry will also be given.

The following lectures on Metallurgy will be given by Mr. Read:—10 lectures on Fuel; Fee, 10s. 6d. 20 lectures on General Metallurgy; Fee, £1 1s. 30 lectures on the Manufacture of Iron and Steel; Fee, £1 1s. A practical course on Iron and Steel Analysis will also be held, and practical instruction in Dry Assaying will be given in the Metallurgical Laboratory, which is fitted with the necessary furnaces and apparatus.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £3 3s. per session; twelve hours, £2 2s. per term; eighteen hours, £3 3s. per term; twenty-four hours £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students wishing to graduate at a Scottish University, or preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of Wales and of the University of London may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY COLLEGE, BRISTOL.

Professor of Chemistry—Sydney Young, D.Sc., F.R.S.

Lecturer—Francis E. Francis, B.Sc., Ph.D.

Demonstrator—E. B. Ludlam, B.Sc.

The session 1901-1902 will begin on October 8. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratories. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the College. Several Scholarships are tenable at the College. Full information may be obtained from the Secretary.

DAY LECTURES.

Inorganic Chemistry.

The Courses treat of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Elementary Course.—Two Lectures a week will be given during the Session. Fee, £4 4s.

General Elementary Science (London Matriculation).—A course of about 16 Lectures will be delivered in the Third Term. Fee, including Physics (1st and 2nd Terms), £5 5s.

Special Course.—A special course of Lectures is also given to Engineering Students.

Intermediate Course.—Three Lectures a week will be given throughout the Session. Fee, £5 5s. There will be tutorial classes in connection with the Elementary and Intermediate Courses.

Advanced Course (Parts I. and II.).—One Lecture a week in each part will be given throughout the Session. Fee for each course, £2 12s. 6d.

Organic Chemistry.

This Course will relate to the more important groups of the Compounds of Carbon.

Two Lectures a week will be given throughout the Session. Fee, £3 3s. An advanced course of lectures will also be given one day a week during the session. Fee, £2 12s. 6d.

Practical Chemistry.—Laboratory Instruction.

The Laboratory will be open daily from 10 a.m. to 5 p.m., except on Saturdays, when it will be closed. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, Metallurgy, and Inorganic and Organic Research. Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures. Fees in Guineas—

	5 Days a Week.	4 Days a Week.	3 Days a Week.	2 Days a Week.	1 Day a Week.
Per Session	15	12½	10	7½	5
„ Two Terms ..	11	9	7½	5½	3½
„ One Term ..	7	6	4½	3½	2½

Students may arrange to divide their days of laboratory work into half-days.

Chemical Scholarship.—Among others, a Chemical and a Metallurgical Scholarship each of £25 are offered for competition.

Evening Lectures.

Two courses of Lectures will be delivered during the First and Second Terms; they will be devoted to the consideration of the general Principles of Chemistry and Chemical Physics and the Chemistry of Non-Metallic and Metallic Elements. Special attention will be paid throughout to those products which have a practical application in the Arts and Manufactures. Fee for each course, 7s. 6d.

General Elementary Science.—A course of Lectures, primarily intended for Candidates for Matriculation, will be given during the First Term. Fee (including Physics), 7s. 6d.

Practical Chemistry — Laboratory Instruction. — The Laboratory will be open two evenings a week from 7 till 9. Instruction will be given in Qualitative and Quantitative Analysis, and in the Preparation of Chemical Products. Fees:—(Two Terms) Two Evenings, 25s.; One Evening, 15s. (One Term) Two Evenings, 15s.; One Evening, 10s. 6d.

University College, Bristol, has been approved by the Council of the Institute of Chemistry as a College at which all the subjects required for the admission of Associates to the Institute are taught.

The Calendar of the College, price 1s. (post-free, 1s. 4d.), containing detailed information of the various Courses, may be obtained on application to the Secretary.

MERCHANT VENTURERS' TECHNICAL COLLEGE, BRISTOL.

Chemistry and Metallurgy.

Professor—J. Wertheimer, B.Sc., B.A., F.I.C., F.C.S.

Lecturers—G. P. Darnell-Smith, B.Sc., F.I.C., F.C.S; A. E. Thomas, B.Sc., F.I.C., F.C.S.; H. A. M. Borland, A.R.C.S.

Demonstrators—F. B. Gatehouse; W. H. Collier (of the University of London).

Assistant in Chemical Laboratory—C. E. Young.

The Laboratories of this Department are open during the Term on every week-day as a School of Practical Chemistry, Analysis, and Assaying, to Students of either sex. They include the Junior Laboratory (for forty Students working at one time), Senior Laboratory, Gas Analysis Room, Balance Room, Combustion Room, Store Rooms, and Metallurgical Laboratory. Each Student works independently, and receives individual instruction and help.

The training in this Department is intended to fit Students to become Professional Chemists, to prepare them for Medical or Pharmaceutical examinations in Chemistry, to instruct them in the branches of Applied Chemistry required in Manufactures and Agriculture, and to train them in practical Metallurgical processes, especially Assaying.

Special facilities will be given to Students wishing to undertake research work approved by the Principal; and the Courses provide completely for the Preliminary Scientific Examination (M.B.), and for the Examinations in Chemistry for the B.Sc. degree of the University of London.

The three years' course at this College in the subjects of Theoretical and Practical Chemistry, Theoretical and Practical Physics, and Elementary Mathematics, is accepted by the Council of the Institute of Chemistry as satisfactory evidence of the training of candidates for the Associateship of the Institute, provided the details in each case be certified by the Professors.

Certificates of Proficiency in Assaying will be given to Students who complete a Course of not less than two years' work in the Metallurgical Department, and pass satisfactorily the College examinations in the Theory and Practice of Assaying.

The Laboratories are open every week-day from 9 till 12 noon, and from 1.30 to 4.30 p.m., except Saturday, when they close at noon.

The Annual Fee of £10 10s. secures (in addition to the use of either or both Laboratories) permission to attend the Lectures in Physics and Mathematics as well as Chemistry, and to use the Physical Laboratory and the Engineering Workshop.

The College Evening Classes, available to persons of either sex, will commence on Monday, September 30th.

Further detailed information may be obtained from the College Prospectus, price 6d.

UNIVERSITY OF BIRMINGHAM.

Professor—Percy F. Frankland, Ph.D., M.Sc., F.R.S.
Assistant Lecturer—T. S. Price, Ph.D., D.Sc.
Demonstrator—R. C. Farmer, Ph.D., M.Sc.
Lecturer on Metallurgy—Godfrey Melland, F.I.C.

The Session will be opened on October 1st, 1901.

Lecture Courses.

First Year.—A. This part of the course is arranged (1) to give a full exposition of the general principles of Chemical Science, (2) for the systematic study of the properties of the more important elements and their compounds, and (3) to indicate the chief applications of Chemistry in the Arts and Manufactures. Four hours weekly during the Winter and Spring terms. At least one of the above meetings of the class in each week will be devoted to tutorial work. Attendance at this tutorial class is compulsory, as is the performance of the weekly exercises set by the Professor. Mondays to Fridays inclusive, at 9.30 to 10.30 a.m. Fee, £5 5s. B. This part of the course includes an introduction to the study of Organic Chemistry, with a description of the properties, relations, and methods of preparation of the more important groups of Carbon Compounds. Three hours weekly during the Summer term. Mondays, Wednesdays, and Fridays, at 9.30 to 10.30 a.m. Fee, £1 11s. 6d.

Second Year.—Advanced Organic Chemistry.— This course extends over two years, and is divided into two parts:—(*a*) Carbon Compounds of the Fatty Series; (*b*) Aromatic and other Cyclic Compounds. Only one of these parts will be taken in each year. The class meets twice weekly by arrangement during the Winter and Spring

terms. Fee, £2 2s. *General and Physical Chemistry.*—This course will deal in outline with various Chemical subjects. The class meets once weekly by arrangement during the three terms. Fee, £1 11s. 6d.

Third Year.—A further Course in Advanced Organic Chemistry will deal with one of the above parts of the Course. The class meets two hours weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. A further Course on General, Physical, and Organic Chemistry, in which special subjects attracting attention at the time receive treatment. Fee, £1 11s. 6d.

Practical Chemistry.

The instruction in Practical Chemistry extends over three years. The Laboratory will be open daily from 9.30 to 5, except on Saturdays, when it will be closed at 1 p.m. Fees—

	All day.	Three hours per day.	Three hours per day; five days a week.	Three hours per day; three days a week.
	Guineas.	Guineas.	Guineas.	Guineas.
One Term ..	7	4½	4	2½
Two Terms .	13	8½	7½	5
Three Terms	18	12	11	6½

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Special facilities are given to Advanced Students for the prosecution of original research.

Metallurgy.

Three Courses of Ten Lectures will be given on the Principles and Practice of Metallurgy. Fee, 10s. 6d. for each of the first two courses, and for each of the two sections of the third course. A more advanced course of about sixty lectures upon selected subjects is also given.

There is a separate laboratory for metallurgical students in which provision is made for instruction in assaying, &c

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of about £96 each are awarded annually in September.

Bowen Scholarship.—One Open Scholarship in Metallurgy of the value of about £96 is awarded annually in September.

For particulars apply to the Registrar.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturers.

BRADFORD MUNICIPAL TECHNICAL COLLEGE.

DEPARTMENT OF CHEMISTRY AND DYEING.

Head of Department—W. M. Gardner.

Lecturers in Chemistry—A. W. Gilbody, Ph.D. (Munich), M.Sc. (Victoria); and S. F. Steil, F.C.S.

Lecturer in Dyeing—A. B. Knaggs, F.C.S.

Lecturer in Metallurgy—W. J. Willis.

Lecturer on Botany, Biology, and Pharmacy—W. West, F.L.S., Ex. Pres. Yorkshire Naturalists' Union.

The following courses of instruction are provided:—

I. *General Chemistry Course*, extending over three years, including Lectures in Inorganic, Organic, and Technological Chemistry, Principles of Analysis, Technical Analysis, Chemical Philosophy, Crystallography, Fuels, Lighting and Ventilation, Physics, Mathematics, Mechanics, with Laboratory work in Chemistry, Physics, Bacteriology, and Microscopy.

II. *Chemistry and Dyeing*, extending over three years. Includes most of the above subjects, along with Lectures and practical work in Dyeing, Colour matching, &c.

III. *Chemical Engineering.* Three years' course, preparing Students for positions in Chemical Works, Sewage Works, &c.

IV. *Dyeing.* Extending over one or two years.

V. *Textile and Dyeing.* Arranged for those Students who desire to study the two subjects simultaneously.

VI. *General Pharmaceutical Course.* Prepares for the Minor and Major Pharmaceutical Examinations. Each extends over two years on three half-days per week, and includes Chemistry and Physics, Botany, Biology, Materia Medica, Pharmacy, and Dispensing.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

CHEMICAL DEPARTMENT.

Professor—Prof. E. Kinch, F.C.S., F.I.C.

Assistant—W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation, of stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

VICTORIA UNIVERSITY. THE YORKSHIRE COLLEGE, LEEDS.

Professor of Chemistry—Arthur Smithells, B.Sc. Lond., F.R.S.

Lecturer in Organic Chemistry—Julius B. Cohen, Ph.D.

Assistant Lecturers and Demonstrators—T. S. Patterson, Ph.D.; J. McCrae, Ph.D., and H. M. Dawson, B.Sc., Ph.D.

Demonstrator—H. T. Calvert, B.Sc., Ph.D.

The Session begins October, 1901.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m. Fee for the Course, £4 4s.

2. Advanced Inorganic Chemistry.—Metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.

3. Advanced Inorganic Chemistry.—Non-metals. Tuesday and Thursday at 9.30 a.m. Fee, £3 13s. 6d.

4. Organic Chemistry. — Tuesday, Thursday, and Saturday at 12 noon Fee £3 13s. 6d.

5. Honours Courses—
   - (*a*) Organic Chemistry. — Wednesday and Friday at 12 noon. Fee, £2 12s. 6d.
   - (*b*) History of Chemistry.—Monday and Wednesday at 9.30 a.m. in the First Term. Fee, £1 1s.
   - (*c*) Physical Chemistry.—Tuesday and Saturday at 9.30 a.m. in the Second and Third Terms. Fee, £2 2s.
   - (*d*) Selected subjects.—Thursday at 9.30 a.m. in the Second and Third Terms. Fee, £1 1s.
   - (*e*) Electro-chemistry.—One hour weekly. Fee, £1 11s. 6d.

Laboratory Courses.

The College Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—Students working six days per week, £21; five, £18 18s.; four, £16 16s.; three, £13 13s.

Class in Practical Chemistry, Saturday mornings, from 9.30 to 12.30. Fee £1 11s. 6d.

Practical Course in Sanitary Chemistry.—Tuesdays and Thursdays from 2 to 5 p.m., from January to March. Fee, £3 5s.

Dyeing Department.

Professor—J. J. Hummel, F.I.C.

Lecturer and Research Assistant — A. G. Perkin, F.R.S.E.

Assistant Lecturer—R. B. Brown.

This Course extends over a period of three years, and is intended for those who wish to obtain a full scientific and practical education in the art of dyeing. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, *e.g.*, the sons of manufacturers, calico printers, managers, master dyers, &c.

Leather Industries Department.

Professor—H. R. Procter, F.I.C.

Assistant Lecturer and Demonstrator—Andrew Turnbull, Ph.D.

The full Courses, which extend over a period of either two or three years, are suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and are recommended to sons of tanners. The Courses include instruction in chemistry, a modern language, leather manufacture, and practical work in the Leather Industries Laboratory and Dye-house.

Agricultural Department.

Professor—R. S. Seton, B.Sc.

Lecturer in Agricultural Chemistry—H. Ingle, F.I.C.

The full Course occupies two years, and includes instruction in chemistry, physics, mathematics, geology, botany, forestry, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out door agriculture.

Research Students are admitted to the College Laboratories on reduced terms.

Several valuable Scholarships are at the disposal of the College, viz., the Salt, Akroyd, Brown, Baines, Emsley, Craven, Leeds City Council, and Clothworkers' Scholarships, and one of the 1851 Exhibition Scholarships. The North, East, and West Ridings County Council's Scholarships are tenable at the Yorkshire College.

UNIVERSITY COLLEGE, LIVERPOOL.

Professor—J. Campbell Brown, D.Sc.

Lecturer on Organic Chemistry—A. W. Titherley, D.Sc., Ph.D.

Lecturer on Metallurgy—T. L. Bailey, Ph.D.

Demonstrators and Assistant Lecturers — T. L. Bailey, Ph.D.; A. N. Meldrum, B.Sc.; A. T. de Mouilpied, B.Sc., Ph.D.; and A. W. Titherley, D.Sc., Ph.D.

Assistant—H. H. Froysell.

The Session commences October 3rd.

Entrance Scholarship Examination takes place early in May each year.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D Sc. Degree in Victoria University; for Degrees in Medicine of Victoria, London, and Edinburgh; for the Pharmaceutical Diplomas; for a special Technological Certificate of University College; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry of Great Britain and Ireland, and other Examination Boards.

Lecture Courses.

General Elementary Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, including Practical class, £4.

Pharmacy Courses: Junior, £3; Senior, £3.

Dental Course, Lectures and Practical, Fee, £5 5s.

Course A.—Non-metals. Fee, £3.

Course B.—Metals. Fee, £3.

Course C.—Organic Chemistry. Fee, £3.

Course H.—Special Organic Subjects. Fee, £2.

Course D.—Physical Chemistry, with Practical Work. Fee, £2.

Course E.—History of Chemistry and of the Development of Modern Chemical Philosophy. Three Terms. Fee, £2.

Courses F. — Applied Chemistry and Metallurgy: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) General Principles of Metullurgy. (3) Iron, Steel, and Aluminium. (4) Copper, Lead, Silver, and Gold, and other Metals. (5) Distillation of Coal and Tar Industries. (6) Fuel and Gas. (7) Chemistry Applied to Sanitation. (8) Technical Gas Analysis. (9) Electrochemical work. Three terms. Fee, each course £1 10s.

Practical Classes.

(1) Junior. (2) Intermediate: Qualitative Analysis of Inorganic Substances and of some of the more common Organic Substances; preparation of Inorganic Compounds. (3) Revision Class. (4) Senior: Practical Organic. (5) Practical Exercises on Technology, Pharmaceutical Chemistry, Sanitary subjects, Examination of Water and Air, &c. (6) Quantitative Class.

Chemical Laboratory.

The Chemical Laboratories recently erected provide accommodation for every kind of chemical and metallurgical work and research. They include thirty rooms devoted to the study of Chemistry and Metallurgy. Separate rooms are provided for Organic Work, Quantitative Analysis, Water Analysis, Gas Analysis, Photometry and Photography, Electro-chemical Work, and a Research Laboratory. New stores for students' apparatus and chemicals have also been built and placed in charge of a skilled dealer.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study, for which a full curriculum is provided.

TABLE OF FEES.

Per Week.	One Term, Three Months.	Three Terms, One Session.
One day	£4	£7
Two days	5 10s.	10
Three days	7	13
Whole week	10 10s.	21

Pharmaceutical Course (see special syllabus).

Technological Curriculum.

Preliminary Year.—Chemistry, the Elementary Course. Practical Classes 1 and 2. Mathematics, or Mechanics, Elementary Engineering, Drawing, and Design (in this or one of the following years). German. Or, the Victoria Preliminary Course and Examination may be taken.

First Year.—Chemistry—Courses A and B; Chemical Laboratory three days per week; Technological Chemistry, Course F. Physics, with laboratory work, one day per week. Mathematics (intermediate). German. Engineering, First Year Course, Autumn and Lent Terms. Intermediate B.Sc. Examination may be passed.

Second Year.—Chemistry, Lecture Course C, on Organic Chemistry, Lecture Course D or E, Technological Chemis-

try, Course F. Chemical Laboratory, four days per week. Engineering, Mathematics, or Physics (Advanced). The Final Examination for the Victoria B.Sc., or the Intermediate Examination of the Institute of Chemistry, may be taken.

Third Year.—In the third year the student should begin to specialise. The following are possible alternatives:—1. Courses D, E, and F; Course H. Any other Courses omitted in a previous year. Laboratory, five days per week. The Degree of B.Sc. in the Honours School of Chemistry may be taken. 2. Metallurgical Classes. Metallurgical Laboratory, two days per week. Chemical Laboratory, Gas Analysis, and Electro-chemistry, two days per week. Physical and Electrotechnical Laboratory, one day per week. 3. Courses D, E, and F. Physics (Senior Course). Chemical Laboratory, four days per week. Physical Laboratory, one day per week. 4. Courses D and F, and a course on Chemistry applied to manufacturing operations. Chemical Laboratory, three or four days per week. Engineering Laboratory and Electrotechnical Laboratory, one day per week.

Students may finally choose a special subject either of research or of applied Chemistry. The Final Examination for the Associateship of the Institute of Chemistry may be taken after 1, 2, or 3. Those who have taken the Ordinary Degree of B.Sc. may pass the Victoria M.Sc. Examination in any subsequent year.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1902, on an Examination in subjects which are included in the first two and a half years of the above curriculum. Candidates should send in their names to the Principal not later than November 15, 1902. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

Evening Classes.

Classes, including laboratory work, will be held during the winter.

The Prospectus containing full particulars may be obtained from the Registrar, University College, Liverpool.

DURHAM COLLEGE OF SCIENCE, NEWCASTLE-ON-TYNE.

Professor of Chemistry—P. Phillips Bedson, M.A., D.Sc., F.I.C., F.C.S.

Lecturer in Chemistry—F. C. Garrett, M.Sc., F.C.S.

Lecturer in Agricultural Chemistry—S. Hoare Collins, F.I.C., F.C.S.

Assistant Lecturers and Demonstrators—J. A. Smythe, B.Sc., Ph.D., and H. W. Cousins, B.Sc.

1. *General Course.*—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 10th. Fee, £3 10s. for the Session.

Second Year Course.—The Lectures for the second year students consist of a course of Lectures on Organic Chemistry, and a course of Lectures on Inorganic Chemistry. The class on Organic Chemistry will meet on Tuesdays and Thursdays at 11 a.m., and will commence on October 8th. The class for Inorganic Chemistry meets at 9.15 a.m. on Wednesdays, commencing October 9th. Fee for Session, £3 10s.; for Inorganic alone £1 10s.; and for Organic alone £3.

Advanced Classes will be formed for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for the course, £3 10s.

A Lecture Course in Analytical Chemistry will be given on Fridays, at 9.15 a.m.

Metallurgy and Assaying.—Lecturer, Professor Louis, M.A., F.I.C., F.C.S.; Demonstrator, G. H. Stanley, A.R.C.M. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry Assaying, and in the preparation and analysis of Alloys, &c. Fees as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10s.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working two days, £2 10s. per term, £6 per session; one day per week, £1 10s. per term, £3 10s. per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subject professed in the College as will enable them to pass the Examinations for the title of Associate in Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in reading, writing from dictation, English or Latin Grammar, arithmetic (including decimals), and geography. Registered students in medicine are exempted from this examination, or students who produce a certificate of having passed either of the three following examinations:—

1. The first examination for the Degree of B.Litt.
2. Durham Examination for certificate of proficiency in General Education, held in March and September.
3. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

Associateship in Science.—Every candidate for the Associateship in Science will be required to satisfy the examiners in—Mathematics, Physics, Chemistry, and either Geology or Natural History—in an examination to be held at the end of the candidate's first year, and at the end of the second year in an examination in a more advanced stage in any two of these subjects. Associates in Science are admissible one year after obtaining the title of Associate to the examination for the degree of Bachelor of Science of the University of Durham.

Exhibitions.—Three Exhibitions of the value of £25, £15, and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Monday, September 30th.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Two Exhibitions of £15 each will be awarded at the next examination of "Persons not members of the University," which will be held at Durham in March next.

Several other valuable Scholarships are available for students, including the Johnston Chemical Scholarship of the value of £60 for one year, which is open to Bachelors of Science of any British Universities.

OWENS COLLEGE,
VICTORIA UNIVERSITY, MANCHESTER.

Professor and Director of the Chemical Laboratory—Harold B. Dixon, M.A., F.R.S.

Professor of Organic Chemistry—W. H. Perkin, Ph.D., F.R.S.

Demonstrators and Assistant Lecturers—George H. Bailey, D.Sc., Ph.D.; W. A. Bone, D.Sc.; P. J. Hartog, B.Sc.; D. L. Chapman, B.A.; Norman Smith, B.Sc.; and F. V. Darbishire, B.A., Ph.D.

Demonstrator in Organic Chemistry—W. T. Lawrence, B.A., Ph.D.

Lecturer in Technical Organic Chemistry—Jocelyn F. Thorpe, Ph.D.

Assistant Lecturer in Metallurgy—Dr. Bone.

The Session begins on October 1, 1901.

The instruction is given by means of Experimental Lectures and Tutorial Classes. The Chemical Classes form part of the Courses for Chemistry in the University.

Chemistry Lecture Courses.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 9.30, during Lent Term.

These courses are intended for Medical Students and others beginning the study of chemistry.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30 a.m., during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Tuesdays, Thursdays, Saturdays, 11.30 a.m., during the two Winter Terms. The Metals.

Third Year Honours Course.—At times to be arranged. Physical Chemistry.

Organic Chemistry (*General*).—Mondays and Fridays, 9.30, during two Winter Terms.

Organic Chemistry (*Advanced*).—Tuesdays and Thursdays, 9.30, during the two Winter Terms.

History of Chemistry and Chemical Philosophy.—Wednesdays, 9.30, during the Session.

Metallurgy.—*Lectures*: The Metallurgy of Copper, Lead, Silver, Gold, and the Metallurgy of Iron and Steel will be given in alternate years. *Practical*: The Metallurgical Laboratory will be open to students every day.

Electro-Chemistry.—In connection with the new John Hopkinson Memorial Laboratory, rooms have been fitted for the study of Electricity in its applications to Chemistry. Courses of lectures and laboratory instruction will be given to Advanced Chemical Students in the coming Session. *Lecturer*—R. S. Hutton, B.Sc.

The Chemical Laboratories are open daily from 9.30. a.m. to 4.30 p.m., except on Saturdays, when they are closed at 12.30 p.m.

Courses for B.Sc. Degree.—To qualify for the B.Sc. Degree of the Victoria University, Students have to attend a prescribed course of study extending over three years, and to pass the Preliminary Examination of the University either on entering or at the end of a year's Course.

The Honours Course of Chemistry is as follows:—First year: First year Honours Lectures; Mathematics (3 hours a week); Physics (3 hours a week); a Language (3 hours a week); Chemical Laboratory (3 days per week). Second year: Second year Honours Lectures; General Organic Lectures; Applied Chemistry Lectures; Physics Laboratory (1 day per week); Chemical Laboratory (3 days per week). Third year: Third year Honours Lectures; Honours Organic Lectures; History of Chemistry Lectures; Chemical Laboratory (5 days per week).

The following awards are made to successful Students in the Honours Examination:—A University Scholarship of £50; a Mercer Scholarship of £25. A University Fellowship of £150 is awarded annually among the Graduates in Science for the encouragement of Research. Among the *College* Scholarships open to Chemical Students are the Dalton Chemical Scholarship, £50 per annum for two years; the 1851 Exhibition Scholarship; &c.

Applied Chemistry.

First Course.—Sulphuric Acid and Alkali Manufactures. General Principles of Chemical Engineering.

Second Course.—The Chemistry of Fuel. The Manufacture of Illuminating Gas and Gaseous Fuel.

Third Course.—Natural and Artificial Dye-stuffs, and the Principles of Dyeing and Printing.

Certificates in Applied Chemistry.

The course extends over a period of three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

Before admission to the first year's course students are required to give such evidence of elementary knowledge of Mathematics and Chemistry as shall be considered satisfactory by the Senate.

The first year's course is the same for all students working for the certificate.

In the second and third years a choice may be made between Inorganic and Organic Chemistry. By this division of the subject a student wishing to apply himself specially to the inorganic side of the science, may attend during his second year the Honours course in Metals, and courses on Geology or Mineralogy, and during his third year, courses on Metallurgy and on Geology or Mineralogy; while a student wishing to apply himself specially to the organic side of the science, may attend during his second and third years the Courses on Organic Chemistry, and courses on the Coal Tar Colours and on Dyeing and Printing.

Part of the Laboratory practice in the second and third years will consist in the examination and analysis of raw materials, products from chemical works, &c., in connection with the special courses of lectures on Applied Chemistry. In the Chemistry and Physical laboratories the practical work in the second year will be arranged in accordance with the branch of Chemistry selected by the candidate.

In the third year the student, if sufficiently advanced, will be set to work on some analytical process or problem in Applied Chemistry, under the direction of the teaching staff.

Electro-chemical Laboratory.

In the new Physical laboratories, arrangements have been made for a complete equipment for Electro-chemical and Electro-metallurgical work. Professor of Physics and Director of Physical Laboratories, Arthur Schuster, Ph.D., F.R.S.; Professor T. H. Core, M.A.(Edin.). Lecturer and Assistant Director of Laboratories, Charles H. Lees, D.Sc.(Vict.). Demonstrator and Assistant Lecturer in Electro-technics, Robert Beattie, B.Sc. (Durham). Demonstrator and Assistant Lecturer in Electro-chemistry, R. S. Hutton, M.Sc (Vict.). Assistant Demonstrators, James Lord, B.Sc.(Vict.); R. C. Wale, B.Sc.(Vict.).

For further particulars apply to the Registrar, Mr. S. Chaffers.

UNIVERSITY COLLEGE, NOTTINGHAM.

Departments of Chemistry and Metallurgy.

Professor of Chemistry—F. Stanley Kipping, Ph.D., D.Sc., F.I.C., F.R.S.

Demonstrators of Chemistry—R. M. Caven, B.Sc., F.I.C.; G. D. Lander, D.Sc.; and G. Sand, Ph.D., M.Sc.

The Classes of the College are open to students of both sexes above sixteen years of age.

The Session commences on October 7th. Evening Classes begin September 23rd.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Elementary Inorganic Chemistry. In his second year he attends Lectures on both Inorganic and Organic Chemistry. In his third year he attends courses on Advanced Organic Chemistry, Physical Chemistry, and Advanced Inorganic Chemistry.

The fees for the Day Lectures and Classes are as follows: First year, two Lectures per week, 15s. per term.

Second year, three Lectures per week, 22s. 6d. per term. Third year, four Lectures per week, 30s. per term.

Demonstrations and Lectures on Analytical Chemistry are given, and Chemical Calculation and Tutorial classes are also held. Various short courses of lectures on Electrochemistry and other special subjects are delivered during the Session.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh; they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry and Metallurgy.—The Chemical and Metallurgical laboratories are open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1; also on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Metallurgy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees for day students: For one term, £7; for the session, £18; for six hours weekly 40s., and 5s. extra for each additional hour per week. For evening students, 10s. for two hours per week, three hours 15s., four hours 20s., per term.

Research Work.—Students or others wishing to undertake research work in pure or Applied Chemistry will be afforded every facility for doing so and may be admitted at reduced fees. The Laboratories are fully equipped with apparatus and chemicals necessary for such work.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students are provided with Lectures and Laboratory work suitable for the preparation for the Minor and Major Examinations. Special lectures will also be given in Pharmacy, Materia Medica, and all other Pharmaceutical subjects.

Evening Classes.—Evening Lectures and Laboratory instruction will be given in Pure and Applied Chemistry, and the laboratories are open for practical work on Tuesday and Thursday evenings from 7 to 9. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

Full information concerning all College Classes is given in the College Prospectus, price one penny.

UNIVERSITY COLLEGE, SHEFFIELD.

Professor of Chemistry—W. Carleton Williams, B.Sc., F.C.S.

Lecturer—G. Young, Ph.D., F.R.S.E.

Demonstrator—T. Slater Price, D.Sc.

The Session will commence on October 2nd.

Beginners' Course.—Inorganic Chemistry: Thursday from 10 to 11 a.m. Fee, £1 11s. 6d.

Matriculation Course.—Tuesday and Friday 10 to 11. Fee, £2 2s.

Intermediate Course.—Inorganic Chemistry. Monday and Thursday from 10 to 11 a.m. £2 12s. 6d.

Organic Chemistry.—Elementary: Saturdays, 10 to 11; fee, £1 11s. 6d. Honours: Tuesdays and Thursdays, 12 to 1; fee, £2 12s. 6d. Advanced: Thursdays, 4 to 5; fee, £1 11s. 6d. Special Course: Hours to be arranged; £1 1s

Physical Chemistry.—Tuesday, 11 to 12. Fee, £1 11s. 6d.

Chemical Philosophy.—Thursday, 11 to 12. Fee, £1 11s. 6d.

Short Courses of Lectures are also given by L. T. O'Shea on the Chemistry of Coal Mining.

A Course of Lectures is arranged for Medical Students, with a special class in Qualitative Analysis.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Six hours per week, £5 5s.; Nine, £7; Twelve, £8 8s.; Eighteen, £11 5s.: Twenty-four, £14; Thirty-two, £17.

Day Students may not enter for less than six hours a week. Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

Fees for short periods (working thirty-two hours per week):—For one month, £3 3s.; two months, £5 5s.

A course of Elementary Practical Physics and Practical Chemistry, which will meet the requirements of candidates for the Diploma of Public Health and for the Licentiate of Sanitary Science, will be held during the Michaelmas and Lent terms. Fee £5 5s.

An arrangement has been entered into with the Science and Art Department, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Department being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Evening Classes.—Lectures, Wednesday, 8 to 9. Laboratory instruction, Wednesday, 6 to 9, and another series to be arranged if desired. Sessional Fee, one evening per week, £1 10s.; or Lecture Class and Laboratory, on Wednesday evening, £1 10s. Fee for one term, 17s. 6d.

Department of Metallurgy.

Professor of Metallurgy—J. O. Arnold. This Department has been equipped to meet the requirements of the local industries. The Laboratory is fitted with the most modern apparatus for metallurgical analysis, more especially with appliances for the rapid and accurate chemical examination of Iron and Steel, Fuel, and Refractory materials. It also contains a complete pyrometric installation, and a new laboratory for the study of the micrographic analysis of metals has been completed and fully equipped with specially designed microscopes by Ross, polishing tables, etching appliances, incandescent light for evening work, &c. The School is now the most complete of its kind for teaching the practical manufacture, the chemical constitution, and the physical properties of Steel. Special attention is given to the determination of the microscopic constituents of Steel. Although the chief industry of the district occupies the central position in the course of instruction, general metallurgy is not neglected, but is dealt with in a separate syllabus, dealing with metals (other than iron and steel) used in the arts. Students are thus enabled to select and at once enter upon a course of scientific metallurgical training of immediate practical utility. They may take up and work through any portions of the course, but certificates will be granted only to those who follow the prescribed courses, and pass the necessary examinations. Lectures on Iron and Steel Manufacture, on Fuel and Refractory Materials, and on General Metallurgy. Practical Metallurgy:—Laboratory, Furnaces, Foundry, and Testing Machine Course; Practical Course of Metallurgy other than Iron and Steel; Practical Fuel Course for Students engaged in Collieries or Gas-Works.

UNIVERSITY COLLEGE, DUNDEE.

University of St. Andrews.

Professor of Chemistry—James Walker, Ph.D., D.Sc., F.R.S.

Assistant Lecturers—J. S. Lumsden, Ph.D., D.Sc., and J. K. Wood, M.Sc.

Lecture Assistant and Laboratory Steward—J. Foggie, F.C.S.

The Winter Session begins on October 18th, and ends on March 19th. The Summer Session extends from the middle of April to the end of June.

The Junior Lecture Course on Systematic Chemistry is given daily during the Winter Session, and embraces the Elements of Inorganic and of Organic Chemistry.

Advanced Courses, of about fifty lectures each, will be given during the year as follows:—

Organic Chemistry; Inorganic Chemistry, including the more important technological applications; Theoretical and Physical Chemistry; Bleaching and Dyeing, including the Chemistry of the Textile Fibres.

Practical Instruction in all of the above branches will be given in the Laboratories and Dye-house. Special facilities are afforded to Research Students.

UNIVERSITY OF ABERDEEN.

Chemistry.

Professor—Francis R. Japp, M.A., LL.D., F.R.S.

Demonstrators—W. B. Davidson, M.A., D.Sc., and W. Maitland, B.Sc.

I. *General Lecture Course* (100 *Lectures*),—Daily during the Winter Session. The subjects treated of include (1) The Laws of Chemical Combination and the General Principles of Chemistry; (2) Non-metallic and Metallic Elements, and their Compounds; (3) Organic Chemistry; (4) Applications of Chemistry to the Arts and Manufactures. Fees, for first attendance, £3 3s.; for subsequent attendance, £2 2s. A Tutorial Class (without fee), conducted by the Senior Demonstrator, is held in connection with this course.

II. *Special Lecture Course on Organic Chemistry* (50 *Lectures*).—Daily during the Summer Session. Fee, £2. 2s.

III. *Practical Course for Medical Students.*—This course, which occupies five hours a week during the Summer Session—in all fifty hours—is devoted to practice in Elementary Qualitative Analysis. Fee, £3 3s.

IV. *Chemical Laboratory.*—The Laboratory is open to Students daily from 9 a.m. to 5 p.m. Each Student on entering is allowed to arrange his hours of work so as to suit his own convenience, but must adhere to these hours when once fixed. The Laboratory instruction includes: (1) General experiments; (2) Preparations; (3) Qualitative analysis; (4) Quantitative analysis: gravimetric, volumetric, and gasometric. Fee, £3 3s. a session. A certain number of free places are available, on the recommendation of the Professor, and subject to the approval of the Senatus, for research students.

In connection with the Laboratory work, three Lectures a week on Physical Chemistry and selected portions of Inorganic Chemistry are delivered during the Winter Session by the Lecturer, Dr. W. B. Davidson. Fee, £2 2s.

Agricultural Chemistry.

Lecturer—James Hendrick, B.Sc., F.I.C.

This course is given during the Winter Session, and includes both Lectures and Laboratory work. The Lectures deal with the chemistry of the atmosphere, the soil, manures, and foods. The physiological chemistry of plants and animals, the composition and manurial requirements of crops, and dairy chemistry, are also treated of. The Laboratory work is primarily intended to accompany and illustrate the Lectures. Exercises dealing with the properties and composition of soils, manures, feeding stuffs and waters, and with the impurities and adulterations of these, occupy much of the time given to practical work. The fee for the whole course—lectures and practical work—is £3 3s.

UNIVERSITY OF EDINBURGH.

Department of Chemistry.

Professor—Alex. Crum Brown, M.D., D.Sc., F.R.S.

Lecturers—L. Dobbin, Ph.D., and H. Marshall, D.Sc.

Assistants—W. W. Taylor, M.A., D.Sc., J. P. Longstaff, B.Sc., and James Kerr, B.Sc.

The working terms are—Winter Session, from middle of October to middle of March; Summer Session, from beginning of May to middle of July.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical and science students is given by the Professor. The class meets daily; fee £4 4s. An Advanced Course of twenty-five lectures is also given in the Winter Session; fee, £2 2s. A class on Organic Chemistry is held in summer; fee, £2 2s. There is also a class on Chemical Theory, by Dr. Dobbin; fee £1 1s.: and a class on Mineralogy and Crystallography, by Dr. Marshall; fee, £2 2s. All these Lectures, except the General Course, are now open to women.

In addition to the above, Lecture Courses are from time to time given by the Assistants on particular branches of Organic and Inorganic Chemistry. These Lectures are free to Laboratory Students.

Tutorial classes are held in connection with the General Course.

Laboratories.—Practical classes for Medical Students meet daily during the latter part of the Winter Session and in the Summer Session. (Fee, £3 3s.) The laboratories for analytical and advanced practical work are open daily from 9.30 till 4.30. (Fees: Whole Day—Winter Session, £10 10s.; Oct.-Dec., Jan.-March, or Summer Session, £5 5s. Half Day—Winter Session, £6 6s.; Oct.-Dec., Jan.-March, or Summer Session, £3 3s. Preference will be given to students in the above order. Students who are not Matriculated may attend the Chemical Laboratory on payment of the entrance fee of 5s. in addition to the Laboratory fees. Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry, including Gas Analysis, Metallurgy, and Assaying. Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical languages, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Final B.Sc. Examination includes any three or more of the following subjects:—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy, including Anthropology, Physiology, Geology, including Mineralogy, Zoology, including Comparative Anatomy, and Botany, including Vegetable Physiology. In the Final Examination two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed; the same regulations apply also to the Practical and Oral Examinations. Chemistry in this examination embraces Inorganic, including Mineralogical, Chemistry; Organic Chemistry; Chemical Crystallography; History of Chemistry. In the written papers a choice of questions is allowed, so as to adapt the examination to the various courses of advanced study which candidates may have selected. Practical Examination:—Complex Qualitative Analysis; Inorganic Preparations; Gravimetric and Volumetric Analysis. Each candidate taking the higher standard will also be examined on Organic Preparations, Ultimate Organic Analysis, and one of the

following subjects, selected by himself:—Gas Analysis; Assaying; Physico-chemical Measurements.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry may be required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—A. P. Laurie, M.A., D.Sc., F.R.S.E.

Professor—John Gibson, Ph.D., F.R.S.E.

Assisted by the following Lecturers and Demonstrators:—Archibald Boon, B.Sc.; Andrew F. King, F.I.C.; and P. Longstaff, B.Sc.

The Session begins September 30th, 1901.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

The Chemistry Course is designed to meet the wants of Manufacturing Chemists. The instruction consists of Courses in Chemistry, Physics, Mathematics, Engineering, and Mechanical Drawing, with Special Courses in Gas and Paper Manufacture, Brewing, &c., by Experts, in the third year. Special attention will be paid to Electrochemistry. The Chemistry Classes are recognised by the University as qualifying for the B.Sc., in Chemistry.

Matriculation Fee, 5s.; Composition Fee for Engineering Courses, £10 10s.; for Chemistry Courses, £10 10s., £12 12s., £15 15s. Full particulars are published in the Calendar of the College early in September.

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

Professor of Chemistry—G. G. Henderson, D.Sc., M.A.

Professor of Metallurgy—A. Humboldt Sexton, F.C.S., F.R.S.E.

Also, Professors and Lecturers in the other leading branches of Pure and Applied Science and Technology.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan's Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments.

Complete courses of instruction are provided in both Day and Evening Classes.

Copies of the Calendar for 1901-1902 may be had from Mr. H. F. Stockdale, the Secretary, 38, Bath Street, Glasgow, price by post, 1s. 4d. Prospectuses will be sent free.

UNIVERSITY OF ST. ANDREWS.

UNITED COLLEGE OF ST. LEONARD AND ST. SALVATOR.

Professor of Chemistry—T. Purdie, B.Sc., Ph.D., LL.D., F.R.S.

The Session begins on October 9th. A Competitive Examination, open to intending Students of Arts, Science, and Medicine, for about forty Entrance Bursaries, ranging in value from £40 to £10 each per annum, will be held on September 27th and following days. Twenty-six of these Bursaries are restricted to Men and about fourteen to Women, the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine. One Scholarship in Chemistry of the value of £80, tenable for one year, will be open for competition to Graduates of Science at the close of Session 1901-1902.

A Hall of Residence is provided for Women Students.

Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree; the regulations will be found in the "University Calendar."

Lecture Courses.

Two distinct Courses of Lectures are given, each comprising at least one hundred meetings of the class.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment.

This course of instruction is intended to meet the requirements of the M.A., First Science, and M.B., Ch.B. Examinations, so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part to General and Physical Chemistry, the instruction in general being such as is required for the Second B.Sc. Exam.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £3 3s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis; (3) Original Investigation. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the Examinations in Arts, Science, and Medicine.

The fees for Practical Chemistry vary according to the number of hours taken weekly. A certain number of working places in the Laboratory will be available without fee for students who are capable of undertaking original investigation.

QUEEN'S COLLEGE, BELFAST.

Professor—E. A. Letts, Ph.D., D.Sc., F.R.U.I., F.R.S.E., &c.

I.—*Chemistry.*—The lectures are delivered at 3 p.m., on the first five days of each week, and terminate at the end of March. The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry. Fee, £2.

II.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of conducting Chemical Analyses. Fee, £3.

III. *Laboratory Pupils.*—The Chemical Laboratory

is open from November until the end of March, and from May 1st until the third week of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

The new Chemical Laboratories are now open, and are provided with all modern appliances. Special facilities are offered to those engaged in Research work.

Scholarships.—The following College Scholarships are awarded specially in connection with the schools of Chemistry and Physics:—Senior Scholarships in Chemistry alone awarded annually of £40, and tenable for one year. Andrews Studentship in Chemistry and Physics, value about £80 annually, and tenable for two years. 1851 Exhibition Scholarships: One of these Scholarships has hitherto been placed at the disposal of the College every two years, of the annual value of £150, tenable for two or under special conditions for three years.

The following Scholarships, &c., of the Royal University of Ireland are awarded in the same group of subjects (Chemistry and Physics):—At the B.A. Degree examination, First-class Exhibitions of £42 each and Second-class Exhibitions of £21. At the M.A. Degree examination, a Studentship of £100 per annum, tenable for three consecutive years. Also a Junior Fellowship, tenable for four consecutive years, of the annual value of £200.

QUEEN'S COLLEGE, CORK.

Professor—Augustus Edward Dixon, M.D.

Demonstrator—Robert Elliott Doran, F.C.S.

The College Session begins on October 15th, 1901, and ends on June 14th, 1902. The classes are open to male and female students.

Systematic Chemistry.—(1) General course of Inorganic Chemistry, Elementary Organic Chemistry, and Chemical Philosophy.—Fee for each Sessional Course, £2. Each subsequent Course, £1. (2) Advanced Organic Chemistry, and Chemical Philosophy.

Practical Chemistry.—(1) Two ordinary Courses of Practical Chemistry will be held, each of three months' duration; one commencing on January 6th, 1902, and adapted to the requirements of Students proceeding to the Examinations of the Royal University of Ireland; the other ending about the third week in June, and suitable for Medical Students intending to present themselves for the Examinations of other Licensing Bodies. Fee for each Sessional Course, £3. (2) A Course for Pharmaceutical Students will be held in the second and third terms; fee, £5. (3) Special Courses.

The Chemical Laboratory is open daily from 10 to 4 o'clock (except during class hours and on Saturdays) under the Superintendence of the Professor, to Students entering for special courses of qualitative and quantitative analysis; organic chemistry; or for the purpose of original investigation.

QUEEN'S COLLEGE, GALWAY.

Professor—Alfred Senier, Ph.D., M.D., F.I.C., F.C.S.

Demonstrator—William Goodwin, F.C.S.

The College Session commences in October and ends in June.

Chemistry is studied by attendance at Lectures, by work in the Laboratories, and by the use of the College Library. The Courses in the several faculties are arranged with a view to the requirements of the Royal University of Ireland, but are adapted also to those of other Universities and licensing bodies.

Lecture Courses. Faculty of Arts.—1. Second year's Course, Inorganic and the Elements of General Chemistry. 2. Third year's Course, Advanced Organic Chemistry. 3. Fourth year's Post-Graduate Course, Advanced General Inorganic and Organic Chemistry. *Faculty of Medicine.*—First year's Course, Inorganic and Elementary Organic Chemistry. *School of Engineering.*—First year's Course, Inorganic Chemistry.

Laboratory Courses. Faculty of Arts.—1. Second year's Course, Exercises in Inorganic Qualitative Analysis. 2. Third year's Course, Quantitative Analysis and other experiments to suit the requirements of individual Students. 3. Fourth year's Post-Graduate Course, Advanced Quantitative Analysis, Organic and Inorganic Preparations, and determination of their Physical and Chemical characters. 4. The Laboratories are also open to Students for work in other branches of Chemistry. *Faculty of Medicine.*—1. Second year's Course, Inorganic and Organic Elementary Qualitative Analysis, and the Chemical Examination of Urine. *School of Engineering.*—1. Second year's Course, Inorganic Qualitative Analysis.

A Scholarship in Chemistry is offered for competition each year of the value of £40, and Chemistry enters into the subjects required for numerous Scholarships in Arts, Medicine, and Engineering. The Royal Commission for the Exhibition of 1851 offer a Scholarship of £150 per annum. This Scholarship has just been awarded for the second time to a Chemistry Student of this College.

For Fees, Regulations as to Scholarships, and other particulars apply to the Registrar, from whom the Calendar, published in December, and the Extracts from Calendar, published in advance in July, may be obtained.

ROYAL COLLEGE OF SCIENCE, DUBLIN.

Professor of Chemistry—W. N. Hartley, F.R.S.

Assistant Chemist—J. Holms Pollok, B.Sc.

Demonstrator of Chemistry and Assaying—A. E. B. Manders.

The Royal College of Science supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Engineering, and Manufactures, Physics, and Natural Science. If accompanied by a certificate from the Professor of Chemistry, the Diploma of Associate of the Royal College of Science in the Faculty of Manufactures is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry; (2) Advanced Chemistry, including Organic Chemistry; (3) Analytical and Experimental Chemistry; (4) Instruction in Chemical Research.

Fees payable by Non-Associate Students:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£5 for three months; £9 for six months; £12 for the entire session. For Assaying—£5 for three months; £9 for six months £12 for the entire session.

The following are supplementary courses of instruction:—

(1) Laboratory Instruction in the Theory of Chemistry. (2) An Analytical Course for Students in Engineering. (3) A Course of Practical Chemistry for Medical Students. (4) The Analysis of Water, Air, Food, and Drugs, intended for the instruction of Public Analysts and Medical Officers of Health. (5) A Course of Chemistry for Pharmaceutical Students.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

CITY AND GUILDS OF LONDON INSTITUTE FOR THE ADVANCEMENT OF TECHNICAL EDUCATION.—The operations of the City and Guilds of London Institute are divided broadly into four branches: the educational work of three London Colleges, and of the Technological

Examinations. Programmes of the London Colleges may be had on application to the Head Office of the Institute, Gresham College, Basinghall Street, London, E.C., or from the respective Colleges. The Technological Examinations (Examinations Department, Exhibition Road, S.W.), are conducted once every year at various centres throughout the kingdom. Programme, with Syllabus of Subjects, &c., may be obtained of Messrs. Whittaker and Co., Paternoster Square, London, or through any bookseller, price 1od., net. — *City and Guilds Technical College, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph.D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of productive industry, whether Manufactures or Arts. The main purpose of the instruction given is to practically demonstrate the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons who are training to become Technical Teachers; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. The Matriculation Examinations begin on Tuesday, September 17th, and the Winter Session opens on Tuesday, October 1st. *City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in special subjects. An examination for the admission of Students will be held at the College on Tuesday, September 17th. Session begins October 1st. *South London Technical Art School.*—Classes in Modelling, Design, Drawing and Painting, House Decoration.

City of London College, White Street, Moorfields. —Courses of Evening Lectures and Laboratory Practice in Chemistry and Physics, conducted by Mr. I. S. Scarf, F.I.C., F.C.S., assisted by Messrs. H. W. Harrie, F.C.S., and C. A. West, F.C.S., &c. Session commences Sept. 30.

Battersea Polytechnic.—Principal, Mr. Sidney H. Wells, Wh. Sc. Inorganic, Organic, and Technological Chemistry, Mr. John Wilson, M.Sc. (Vict.), assisted by Mr. John L. White, M.Sc., Mr. H. G. Wayling, B.Sc., and Mr. B. C. Polkinghorne, B.Sc. Day and Evening Classes in Science and Art subjects. Session opens Sept. 16. The principal work of the Institute is the provision of Evening Classes for both sexes in all subjects of Technology, Pure and Applied Science, Art, Commerce, Domestic Economy, and Music; but it also provides a Technical Day School, a Science Day School for Boys and Girls, a Training School of Domestic Economy, a Domestic Economy School for Girls, a Day School of Art, and Special Day Courses in Science and Technical subjects. During the last Session, 250 Evening Classes in more than 100 different subjects were attended by over 3100 individual students, while 520 students were in regular attendance at the Day Schools and Classes.

Birkbeck Literary and Scientific Institution, Breams Buildings, Chancery Lane.—Chemistry Courses will be conducted, commencing Monday, September 30, adapted for the Elementary, Advanced, and Honours Examinations of the Science and Art Department, and for the Matriculation, B.Sc., and M.B. Degrees of the London University, by Mr. J. E. Mackenzie, Ph.D., D.Sc. This Institution, which has now completed seventy-eight years of educational work in the metropolis, commences its new Session on Monday, September 30th. The Day and Evening courses of study, comprise the various branches of Natural Science, Mathematics, classical and modern Languages, Economics, Commercial Subjects, Law, Mental Science, Music, and Art. The courses provide for the Examinations of the University of London, in the faculties of Arts, Science, and Commerce, those of the Conjoint Board, Civil Service, &c. The Report for the last session shows that during the year 70 students passed some university examination, while large numbers gained successes at various public examinations. The Institution has had many additions to its appliances in recent years, and the Physical, Chemical, Biological, and Metallurgical laboratories are now very thoroughly equipped. The Day classes provide courses in Chemistry, Biology, Physics, Mathematics, and Geology for the Science Degrees of London University. There are also Day classes in modern Languages, including Russian and Spanish; courses of Lectures on French and German Literature are given both in the afternoon and evening, and also a University Extension course on *Dante* and Italian Literature is arranged for the afternoon. The School of Art is open both day and evening. A new reading room, and a new magazine room have recently been provided. The Metallurgical laboratory has been extended and reorganised, and classes are held both in the day and evening. The Calendar supplies complete syllabuses of the classes and full information about the Institution. A popular Lecture or Entertainment is given in the Theatre every Wednesday evening.

Borough Polytechnic Institute, 103, Borough Road (near the Obelisk).—Chemistry: Evening Lectures and Laboratory Work in Inorganic, Organic, and Electro-Chemistry (Session fees, per course, 5s. to 20s.), Dr. F. Mollwo Perkin, assisted by Dr. E. C. Jee. Electricity and Magnetism: Evening Lectures and Laboratory Work (Session fees, per course, 8s. to 10s.), Dr. J. Henderson. Special Evening Courses on Oils and Fats, including Soap and Candle Manufacture, and on Painter's Oils, Colours, and Varnishes. Session opens Monday, September 23, 1901.

Brixton School of Chemistry and Pharmacy, 12, Knowle Road, Brixton, London.—Principal, Dr. A. B. Griffiths, F.R.S.(Ed.). Lectures on Inorganic and Organic Chemistry, Physics, Botany, &c., for Pharmaceutical, Medical, and other students. The benches in the laboratory are fitted with the best appliances. There are courses in Research Work. Full particulars as to fees, &c., may be obtained by writing to the Principal.

South Western Polytechnic, Chelsea, S.W.—Principal, Herbert Tomlinson, B.A., F.R.S. Professor of Chemistry, J. B. Coleman, A.R.C.S., F.I.C. Day and Evening Courses in Theoretical and Practical Chemistry and several branches of Applied Chemistry, including Metallurgy, Oils and Colours, Photography, &c. Special Classes are held for the Matriculation, Intermediate Science, and B.Sc. Examinations of the University of London. Prospectuses of Day and Evening Classes may be obtained from the Secretary, 1d. each, by post 2½d.

The Goldsmiths' Institute, New Cross, S.E.—Head of the Chemistry Department, Arthur Lapworth, D.Sc.(Lond.), F.I.C.; Assistants, Mr. S. J. Peachey and others. Lectures and Practical Classes in General Chemistry and Photography, also in Chemistry applied to other industries, are held in the evenings from 7.15 to 10, and are open to both sexes. Special attention is paid to Technical Laboratory work and the investigation of manufacturing difficulties. Session commences September 23.

East London Technical College, People's Palace, E.—Chemistry: Professor, J. T. Hewitt, M.A., D.Sc., Ph.D.; Demonstrator, F. G. Pope; Assistants, H. A. Phillips and A. J. Turner. Lectures and Practical Classes are conducted in the daytime in connection with the three years' course of the Day Technical College. Evening Classes are also held, offering instruction in the courses of the Science and Art Department and for the examinations of the University of London. The Day College opens on Sept. 9. Evening Classes begin Sept. 24.

Northern Polytechnic Institute, Holloway Road, N.—Head of Chemical Department, Mr. H. Charles L. Bloxam. Assistants, Mr. W. H. Watson, A.R.C.S., Mr. E. A. Jenkinson, A.R.C.S. Lectures and Practical Classes in Elementary, Advanced, and Honours Inorganic and Organic Chemistry are held in the evenings from 6.30 or 7 p.m. to 9.30 p.m., affording instruction in the Courses for the Examinations of the University of London and the Board of Education. The Classes form a Course of Study extending over five Sessions, and are open to both sexes. The Laboratories are open to those wishing to pursue investigations. A reference library is attached to the Chemical Department. Session begins September 23.

Northampton Institute (City Polytechnic), St. John Street Road, E.C.—Principal, R. Mullineux Walmsley, D.Sc., &c. Lecturers in Technical Chemistry: Mr. C. J. Head, F.I.C., &c.; Mr. S. Field, A.R.C.S.; and Mr. G. Naylor. Day and Evening Classes in Electro-chemistry. Electro-plating, Electro-metallurgy, Electrotyping and Stereotyping, and Gold and Silver Assaying. (For full details see Prospectus).

Carpenters' Company Technical Institute, Jupp Road, Stratford, E.—Principal, William Ping. F.C.S. Evening Classes in Theoretical and Practical Chemistry, and in many other Departments of Science and Art. Day Technical School.

University Tutorial College, 32, Red Lion Square, Holborn, W.C.—This Institution contains large Laboratories for Chemistry, Physics, Geology, and other subjects. Classes are specialised for Examinations of London University, but students may take up work for any Examination. The special feature of the College is that work goes on all the year round, thus affording students residing in the Country an opportunity of doing practical work during their Vacations.

Imperial College of Chemistry and Pharmacy, 51, Imperial Buildings, Ludgate Circus.—Mr. F. Davis, B.Sc. An especial course of instruction is given at this College in Pharmacology and Therapeutics, *re* the Institute of Chemistry Examination. Students attending the College visit technical works.

West Ham Municipal Institute.—Principal, Albert E. Briscoe, B.Sc. (Lond.), &c. Chemical Department, Harold A. Auden, M.Sc., &c., assisted by F. H. Streatfeild and H. V. Capsey. Day and Evening Classes, commencing September 21.

South-Eastern Agricultural College, Wye, Kent.—Chemistry: Professor, A. D. Hall, M.A.(Oxon.); Lecturer, E. J. Russell, B.Sc. (Lond.). Next Session begins October 1. The courses of instruction in Chemistry are suitable to students intending to become analysts or assistants in works manufacturing manures, feeding-stuffs, &c. The College possesses new and well-equipped Laboratories for Chemistry, Botany, and Bacteriology. The farm, gardens, and experiment grounds afford material for investigation and research. Fee: £8 6s. 8d. per term admits to all Lecture Courses, &c.

Blackburn Municipal Technical School.—Chemistry: Mr. Robert H. Pickard, D.Sc.(Lond.)., &c., assisted by Mr. W. H. Duckworth, F.C.S., and Mr. H. G. Thompson. Session opens Monday, September 9. Full details of the Classes are given in the "Students' Handbook," which may be had at the Institution (price 1d.).

Storey Institute, Lancaster.—Principal, Wm. French, M.A., F.I.C. Lecturer in Physics, F. E. Rees, B.Sc. Courses arranged in Chemistry and Physics to suit students for B.Sc., &c.

Leeds Technical School (in connection with the Leeds Institute of Science, Art, and Literature), Cookridge Street, Leeds.—Head Master, R. E. Barnett, B.Sc. (Lond.), A.R.C.S. Evening Classes are held in 31 subjects of Science and Technology, among which are:—Chemistry, Inorganic and Organic, Theoretical and Practical, by Mr. R. E. Barnett, B.Sc., A.R.C.S., Mr. J. B. Murray, A.R.C.S., and Mr. T. R. White, B.A.; Metallurgy, Theoretical and Practical, and Iron and Steel Manufacture, by Mr. B. A. Burrell, F.I.C., F.C.S.; Magnetism and Electricity, and Practical Physics, by Mr. J. E. Tindall, B.Sc.; Botany, Lectures and Practical Work, by Mr. N. Walker. Fees:—Lectures, from 2s. 6d. per Session; Laboratory work, from 2s. 6d. Systematic courses arranged for Pharmaceutical Students and for those engaged in Chemical Industries at reduced composition fees. Session commenced Sept. 16th. Prospectuses of various Classes free on application to the Secretary, Mr. Arthur Tait. Calendar of the Institute (163 pp.) post free 4d.

The Municipal Technical School, Princess Street, Manchester.—The new School now in course of completion will be opened in September, 1901. In addition to the ample arrangements provided for Industrial Chemistry, the Committee have decided upon the erection of new building, 1248 square yards in area, for Bleaching, Dyeing, Printing, and Finishing Textile Goods. The new School, it is stated, will be the largest and probably the most completely equipped school in the kingdom.

Institute of Public Health and Technology, Seymour House, Old Trafford, Manchester.—Principals, Charles Estcourt, F.I.C., F.C.S., &c., and Philip Anderson Estcourt, Ph.D. The course of instruction is especially intended for those who require a knowledge of Chemistry and Bacteriology bearing upon Sanitary matters. Chemical Technology is specially taught with a view to enable Medical Men and others engaged in Sanitary matters to understand the operations at the various works which may come under their control. Persons who desire to take up the branch of Chemical Engineering, including Electrical Engineering, will also have special opportunities of pursuing such studies.

Redruth School of Mines, Cornwall.—Principal, J. Paul de Castro, M.A. (Cantab.), A.I.C., F.C.S., assisted by a staff of Mining Engineers and Mine Surveyors. Courses of Practical and Theoretical instruction are given in Inorganic Chemistry, Assaying, Mineralogy, and Blowpipe Analysis, for intending Assayers and Mineral Chemists. Shorter Courses are also held in the above subjects to meet the requirements of intending Mining Engineers, and Prospectors. Practical instruction in Mining given at Pednandrea, the School Mine. Syllabus on application to the Registrar. Session commences Monday, September 11.

Technical Institute, Salford.—Principal, W. Wilson, M.A. Session begins September 11th. Special attention is directed to the Dyeing and Calico Printing Laboratories. Day and Evening Classes in Science subjects. Also School of Art. Particulars free from Secretary.

Wolverhampton Free Library Science and Technical School.—Inorganic and Organic Chemistry, Mr. W. Whitehouse, F.C.S.; Physics, Mr. H. J. Tench; Botany, Mr. Sidney Phillips, Ph.C.; Latin, Mr. F. G. Griffiths, M.P.S. Day Classes in Chemistry and Physics, and Evening Classes in Chemistry, Physics, Botany, French, Latin, &c. Special arrangements are made for the requirements of Pharmaceutical and Medical Students. The School is recognised by the Examining Board of the Royal College of Surgeons and Physicians, as a centre for preparation in Chemistry and Physics. Session commences Monday, Sept. 9th. For other particulars and programme, apply Mr. J. Elliot, Secretary.

THE CHEMICAL NEWS.

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BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

Glasgow, 1901.

INAUGURAL ADDRESS OF THE PRESIDENT, Prof. Arthur W. Rücker, M.A., LL.D., D.Sc., Sec.R.S.

The first thought in the minds of all of us to-night is that since we met last year the great Queen, in whose reign nearly all the meetings of the British Association have been held, has passed to her rest.

To Sovereigns most honours and dignities come as of right; but for some of them is reserved the supreme honour of an old age softened by the love and benedictions of millions; of a path to the grave, not only magnificent, but watered by the tears both of their nearest and dearest, and of those who, at the most, have only seen them from afar.

This honour Queen Victoria won. All the world knows by what great abilities, by what patient labour, by what infinite tact and kindliness, the late Queen gained both the respect of the rulers of nations and the affection of her own subjects.

Her reign, glorious in many respects, was remarkable, outside these islands, for the growth of the Empire; within and without them, for the drawing nearer of the Crown and the people in mutual trust; while, during her lifetime, the developments of science and of scientific industry have altered the habits and the thoughts of the whole civilised world.

The representatives of science have already expressed in more formal ways their sorrow at the death of Queen Victoria, and the loyalty and confident hope for the future with which they welcome the accession of King Edward. But none the less, I feel sure that at this, the first meeting of the British Association held in his reign, I am only expressing the universal opinion of all our members when I say that no group of the King's subjects trusts more implicitly than we do in the ability, skill, and judgment which His Majesty has already shown in the exercise of the powers and duties of his august office; that none sympathise more deeply with the sorrows which two great nations have shared with their Sovereigns; and that none cry with more fervour, "Long live the King!"

But this Meeting of the British Association is not only remarkable as being the first in a new reign. It is also the first in a new century. It is held in Glasgow at a time when your International Exhibition has in a special sense attracted the attention of the world to your city, and when the recent celebration of the ninth jubilee of your University has shown how how deeply the prosperity of the present is rooted in the past. What wonder, then, if I take the Chair to which you have called me with some misgivings? Born and bred in the South, I am to preside over a Meeting held in the largest city of Scotland. As your chosen mouthpiece I am to speak to you of science when we stand at the parting of the centuries, and when the achievements of the past and present, and the promise of the future, demand an interpreter with gifts of knowledge and divination to which I cannot pretend. Lastly, I am President of the British Association as a disciple in the home of the master, as a physicist in a city which a physicist has made for ever famous. Whatever the future may have in store for Glasgow, whether your enterprise is still to add wharf to wharf, factory to factory, and street to street, or whether some unforeseen "tide in the affairs of men" is to sweep energy and success elsewhere, fifty-three years in the history of your city will never be forgotten while civilisation lasts.

More than half a century ago, a mere lad was the first to compel the British Association to listen to the teaching of Joule, and to accept the law of the conservation of energy. Now, alike in the most difficult mathematics and in the conception of the most ingenious apparatus, in the daring of his speculations and in the soundness of his engineering, William Thomson, Lord Kelvin, is regarded as a leader by the science and industry of the whole world.

It is the less necessary to dwell at length upon all that he has done, for Lord Kelvin has not been without honour in his own country. Many of us, who meet here to-night, met last in Glasgow when the University and City had invited representatives of all nations to celebrate the Jubilee of his professorship. For those two or three days learning was surrounded with a pomp seldom to be seen outside a palace. The strange middle-age costumes of all the chief Universities of the world were jostling here, the outward signs that those who were themselves distinguished in the study of Nature had gathered to do honour to one of the most distinguished of them all.

Lord Kelvin's achievements were then described in addresses in every tongue, and therefore I will only remind you that we, assembled here to-night, owe him a heavy debt of gratitude; for the fact that the British Association enters on the twentieth century conscious of a work to do and of a vigour to do it is largely due to his constant presence at its Meetings, and to the support he has so ungrudgingly given. We have learned to know not only the work of our great leader, but the man himself; and I count myself happy because in his life-long home, under the walls of the University he served so well, and at a Meeting of the Association which his genuis has so often illuminated, I am allowed, as your President, to assure him in your name of the admiration, respect, nay, of the affection, in which we all hold him.

I have already mentioned a number of circumstances which make our Meeting this year noteworthy; to these I must add that for the first time we have a Section for Education, and the importance of this new departure, due largely to the energy of Professor Armstrong, is emphasised by the fact that the Chair of that Section will be occupied by the Vice-President of the Committee of Council on Education—Sir John Gorst. I will not attempt to forecast the proceedings of the new Section. Education is passing through a transitional stage. The recent debates in Parliament; the great gifts of Mr. Carnegie; the discussion as to University organisation in the North of England; the reconstitution of the University of London; the increasing importance attached to the application of knowledge both to the investigation of Nature and to the purposes of industry, are all evidence of the growing conviction that without advance in education we cannot retain our position among the nations of the world. If the British Association can provide a platform on which these matters may be discussed in a scientific but practical spirit, free from the misrepresentations of the hustings and the exaggerations of the partisan, it will contribute in no slight measure to the national welfare.

But amid the old and new activities of our meeting the undertone of sadness, which is never absent from such gatherings, will be painfully apparent to many of us at Glasgow. The life-work of Professor Tait has ended amid the gloom of the war-cloud. A bullet, fired thousands of miles away, struck him to the heart, so that in their deaths the father and the brave son, whom he loved so well, were not long divided. Within the last year, too, America has lost Rowland; Viriamu Jones, who did yeoman's service for education and for science, has succumbed to a long and painful illness; and one who last year at Bradford seconded the proposal that I should be your President at Glasgow, and who would unquestionably have occupied this Chair before long had he been spared to do so, has

unexpectedly been called away. A few months ago we had no reason to doubt that George Francis FitzGerald had many years of health and work before him. He had gained in a remarkable way not only the admiration of the scientific world, but the affection of his friends, and we shall miss sadly one whom we all cared for, and who, we hoped, might yet add largely to the achievements which had made him famous.

The Science of the Nineteenth Century.

Turning from these sad thoughts to the retrospect of the century which has so lately ended, I have found it to be impossible to free myself from the influence of the moment, and to avoid, even if it were desirable to avoid, the inclination to look backward from the standpoint of to-day.

Two years ago Sir Michael Foster dealt with the work of the century as a whole. Last year Sir William Turner discussed in greater detail the growth of a single branch of science. A third and humbler task remains, viz.. to fix our attention on some of the hypotheses and assumptions on which the fabric of modern theoretical science has been built, and to inquire whether the foundations have been so "well and truly" laid that they may be trusted to sustain the mighty superstructure which is being raised upon them.

The moment is opportune. The three chief conceptions which for many years have dominated physical as distinct from biological science have been the theories of the existence of atoms, of the mechanical nature of heat, and of the existence of the ether.

Dalton's atomic theory was first given to the world by a Glasgow professor—Thomas Thomson—in the year 1807, Dalton having communicated it to him in 1804. Rumford's and Davy's experiments on the nature of heat were published in 1798 and 1799 respectively; and the celebrated Bakerian Lecture, in which Thomas Young established the undulatory theory by explaining the interference of light, appeared in the *Philosophical Transactions* in 1801. The keynotes of the physical science of the nineteenth century were thus struck, as the century began, by four of our fellow-countrymen, one of whom—Sir Benjamin Thompson, Count Rumford—preferred exile from the land of his birth to the loss of his birthright as a British citizen.

Doubts as to Scientific Theories.

It is well known that of late doubts have arisen as to whether the atomic theory, with which the mechanical theory of heat is closely bound up, and the theory of the existence of an ether have not served their purpose, and whether the time has not come to re-consider them.

The facts that Professor Poincaré, addressing a congress of physicists in Paris, and Professor Poynting, addressing the Physical Section of the Association, have recently discussed the true meaning of our scientific methods of interpretation; that Dr. James Ward has lately delivered an attack of great power on many positions which eminent scientific men have occupied; and that the approaching end of the nineteenth century led Professor Hæckel to define in a more popular manner his own very definite views as to the solution of the "Riddle of the Universe," are perhaps a sufficient justification of an attempt to lay before you the difficulties which surround some of these questions.

To keep the discussion within reasonable limits I shall illustrate the principles under review by means of the atomic theory, with comparatively little reference to the ether, and we may also at first confine our attention to inanimate objects.

The Construction of a Model of Nature.

A natural philosopher, to use the old phrase, even if only possessed of the most superficial knowledge, would attempt to bring some order into the results of his observation of Nature by grouping together statements with regard to phenomena which are obviously related. The aim of modern science goes far beyond this. It not only shows that many phenomena are related which at first sight have little or nothing in common, but, in so doing, also attempts to explain the relationship.

Without spending time on a discussion of the meaning of the word "explanation," it is sufficient to say that our efforts to establish relationships between phenomena often take the form of attempting to prove that, if a limited number of assumptions are granted as to the constitution of matter, or as to the existence of quasi-material entities, such as caloric, electricity, and the ether, a wide range of observed facts falls into order as a necessary consequence of the assumptions. The question at issue is whether the hypotheses which are at the base of the scientific theories now most generally accepted are to be regarded as accurate descriptions of the constitution of the universe around us, or merely as convenient fictions.

Convenient fictions be it observed, for even if they are fictions they are not useless. From the practical point of view it is a matter of secondary importance whether our theories and assumptions are correct, if only they guide us to results which are in accord with facts. The whole fabric of scientific theory may be regarded merely as a gigantic "aid to memory"; as a means for producing apparent order out of disorder by codifying the observed facts and laws in accordance with an artificial system, and thus arranging our knowledge under a comparatively small number of heads. The simplification introduced by a scheme which, however imperfect it may be, enables us to argue from a few first principles, makes theories of practical use. By means of them we can foresee the results of combinations of causes which would otherwise elude us. We can predict future events, and can even attempt to argue back from the present to the unknown past.

But it is possible that these advantages might be attained by means of axioms, assumptions, and theories based on very false ideas. A person who thought that a river was really a streak of blue paint might learn as much about its direction from a map as one who knew it as it is. It is thus conceivable that we might be able, not indeed to construct, but to imagine, something more than a mere map or diagram, something which might even be called a working model of inanimate objects, which was nevertheless very unlike the realities of nature. Of course, the agreement between the action of the model and the behaviour of the things it was designed to represent would probably be imperfect, unless the one were a facsimile of the other; but it is conceivable that the correlation of natural phenomena could be imitated, with a large measure of success, by means of an imaginary machine, which shared with a map or diagram the characteristic that it was in many ways unlike the things it represented, but might be compared to a model in that the behaviour of the things represented could be predicted from that of the corresponding parts of the machine.

We might even go a step further. If the laws of the working of the model could be expressed by abstractions, as, for example, by mathematical formulæ, then, when the formulæ were obtained, the model might be discarded, as probably unlike that which it was made to imitate, as a mere aid in the construction of equations, to be thrown aside when the perfect structure of mathematical symbols was erected.

If this course were adopted we should have given up the attempt to know more of the nature of the objects which surround us than can be gained by direct observation, but might nevertheless have learned how these objects would behave under given circumstances.

We should have abandoned the hope of a physical explanation of the properties of inanimate Nature, but should have secured a mathematical description of her operations.

There is no doubt that this is the easiest path to follow. Criticism is avoided if we admit from the first that we

cannot go below the surface; cannot know anything about the constitution of material bodies; but must be content with formulating a description of their behaviour by means of laws of Nature expressed by equations.

But if this is to be the end of the study of Nature, it is evident that the construction of the model is not an essential part of the process. The model is used merely as an aid to thinking; and if the relations of phenomena can be investigated without it, so much the better. The highest form of theory—it may be said—the widest kind of generalisation, is that which has given up the attempt to form clear mental pictures of the constitution of matter, which expresses the facts and the laws by language and symbols which lead to results that are true, whatever be our view as to the real nature of the objects with which we deal. From this point of view the atomic theory becomes not so much false as unnecessary; it may be regarded as an attempt to give an unnatural precision to ideas which are and must be vague.

Thus, when Rumford found that the mere friction of metals produced heat in unlimited quantity, and argued that heat was therefore a mode of motion, he formed a clear mental picture of what he believed to be occurring. But his experiments may be quoted as proving only that energy can be supplied to a body in indefinite quantity, and when supplied by doing work against friction it appears in the form of heat.

By using this phraseology we exchange a vivid conception of moving atoms for a colourless statement as to heat energy, the real nature of which we do not attempt to define; and methods which thus evade the problem of the nature of the things which the symbols in our equations represent have been prosecuted with striking success, at all events within the range of a limited class of phenomena. A great school of chemists, building upon the thermodynamics of Willard Gibbs and the intuition of Van t'Hoff, have shown with wonderful skill that, if a sufficient number of the data of experiment are assumed, it is possible, by the aid of thermodynamics, to trace the form of the relations between many physical and chemical phenomena without the help of the atomic theory.

But this method deals only with matter as our coarse senses know it; it does not pretend to penetrate beneath the surface.

It is therefore with the greatest respect for its authors, and with a full recognition of the enormous power of the weapons employed, that I venture to assert that the exposition of such a system of tactics cannot be regarded as the last word of science in the struggle for the truth.

Whether we grapple with them, or whether we shirk them; however much or however little we can accomplish without answering them, the questions still force themselves upon us:—Is matter what it seems to be? Is interplanetary space full or empty? Can we argue back from the direct impressions of our senses to things which we cannot directly perceive; from the phenomena displayed by matter to the constitution of matter itself?

It is these questions which we are discussing to-night, and we may therefore, as far as the present address is concerned, put aside, once for all, methods of scientific exposition in which an attempt to form a mental picture of the constitution of matter is practically abandoned, and devote ourselves to the inquiries whether the effort to form such a picture is legitimate, and whether we have any reason to believe that the sketch which science has already drawn is to some extent a copy, and not a mere diagram, of the truth.

Successive Steps in the Analysis of Matter.

In dealing, then, with the question of the constitution of matter and the possibility of representing it accurately, we may grant at once that the ultimate nature of things is, and must remain, unknown; but it does not follow that immediately below the complexities of the superficial phenomena which affect our senses there may not be a simpler machinery of the existence of which we can obtain evidence, indirect indeed but conclusive.

The fact that the apparent unity which we call the atmosphere can be resolved into a number of different gases is admitted; though the ultimate nature of oxygen, nitrogen, argon, carbonic acid, and water vapour is as unintelligible as that of air as a whole, so that the analysis of air may be said to have substituted many incomprehensibles for one.

Nobody, however, looks at the question from this point of view. It is recognised that an investigation into the proximate constitution of things may be useful and successful, even if their ultimate nature is beyond our ken.

Nor need the analysis stop at the first step. Water vapour and carbonic acid, themselves constituents of the atmosphere, are in turn resolved into their elements, hydrogen, oxygen, and carbon, which, without a formal discussion of the criteria of reality, we may safely say are as real as air itself.

Now, at what point must this analysis stop if we are to avoid crossing the boundary between fact and fiction? Is there any fundamental difference between resolving air into a mixture of gases, and resolving an elementary gas into a mixture of atoms and ether?

There are those who cry halt at the point at which we divide a gas into molecules, and their first objection seems to be that molecules and atoms cannot be directly perceived, cannot be seen or handled, and are mere conceptions, which have their uses, but cannot be regarded as realities.

It is easiest to reply to this objection by an illustration. The rings of Saturn appear to be continuous masses separated by circular rifts. This is the phenomenon which is observed through a telescope. By no known means can we ever approach or handle the rings; yet everybody who understands the evidence now believes that they are not what they appear to be, but consist of minute moonlets, closely packed indeed, but separate the one from the other.

In the first place Maxwell proved mathematically that if a Saturnian ring were a continuous solid or fluid mass it would be unstable, and would necessarily break into fragments. In the next place, if it were possible for the ring to revolve like a solid body, the inmost parts would move slowest, while a satellite moves faster the nearer it is to a planet. Now spectroscopic observation, based on the beautiful method of Sir W. Huggins, shows not only that the inner portions of the ring move the more rapidly, but that the actual velocities of the outer and inner edges are in close accord with the theoretical velocities of satellites at like distances from the planet.

This and a hundred similar cases prove that it is possible to obtain convincing evidence of the constitution of bodies between whose separate parts we cannot directly distinguish, and I take it that a physicist who believes in the reality of atoms thinks that he has as good reason for dividing an apparently continuous gas into molecules as he has for dividing the apparently continuous Saturnian rings into satellites. If he is wrong it is not the fact that molecules and satellites alike cannot be handled, and cannot be seen as individuals, that constitutes the difference between the two cases.

It may, however, be urged that atoms and the ether are alleged to have properties different from those of matter in bulk, of which alone our senses take direct cognisance, and that therefore it is impossible to prove their existence by evidence of the same cogency as that which may prove the existence of a newly discovered variety of matter or of a portion of matter too small or too distant to be seen.

This point is so important that it requires full discussion, but in dealing with it, it is necessary to distinguish carefully between the validity of the arguments which support the earlier and more fundamental propositions of the theory; and the evidence brought forward to justify mere speculative applications of its doctrines which might

be abandoned without discarding the theory itself. The proof of theory must be carried out step by step.

The first step is concerned wholly with some of the most general properties of matter, and consists in the proof that those properties are either absolutely unintelligible, or that, in the case of matter of all kinds, we are subject to an illusion similar to that the results of which we admit in the case of Saturn's rings, clouds, smoke, and a number of similar instances. The believer in the atomic theory asserts that matter exists in a particular state; that it consists of parts which are separate and distinct the one from the other, and as such are capable of independent movements.

Up to this point no question arises as to whether the separate parts are, like grains of sand, mere fragments of matter; or whether, though they are the bricks of which matter is built, they have, as individuals, properties different from those of masses of matter large enough to be directly perceived. If they are mere fragments of ordinary matter, they cannot be used as aids in explaining those qualities of matter which they themselves share.

We cannot explain things by the things themselves. If it be true that the properties of matter are the product of an underlying machinery, that machinery cannot itself have the properties which it produces, and must, to that extent at all events, differ from matter in bulk as it is directly presented to the senses.

If, however, we can succeed in showing that if the separate parts have a limited number of properties (different, it may be, from those of matter in bulk), the many and complicated properties of matter can, to a considerable extent, be explained as consequences of the constitution of these separate parts; we shall have succeeded in establishing, with regard to quantitative properties, a simplification similar to that which the chemist has established with regard to varieties of matter. The many will have been reduced to the few.

The proofs of the physical reality of the entities discovered by means of the two analyses must necessarily be different. The chemist can actually produce the elementary constituents into which he has resolved a compound mass. No physicist or chemist can produce a single atom separated from all its fellows, and show that it possesses the elementary qualities he assigns to it. The cogency of the evidence for any suggested constitution of atoms must vary with the number of facts which the hypothesis that they possess that constitution explains.

Let us take, then, two steps in their proper order, and inquire, first, whether there is valid ground for believing that all matter is made up of discrete parts; and, secondly, whether we can have any knowledge of the constitution or properties which those parts possess.

The Coarse-grainedness of Matter.

Matter in bulk appears to be continuous. Such substances as water or air appear to the ordinary observer to be perfectly uniform in all their properties and qualities, in all their parts.

The hasty conclusion that these bodies are really uniform is, nevertheless, unthinkable.

In the first place the phenomena of diffusion afford conclusive proof that matter when apparently quiescent is in fact in a state of internal commotion. I need not recapitulate the familiar evidence to prove that gases and many liquids when placed in communication interpenetrate or diffuse into each other; or that air, in contact with a surface of water, gradually becomes laden with water-vapour, while the atmospheric gases in turn mingle with the water. Such phenomena are not exhibited by liquids and gases alone, nor by solids at high temperatures only. Sir W. Roberts-Austen has placed pieces of gold and lead in contact at a temperature of 18° C. After four years the gold had travelled into the lead to such an extent that not only were the two metals united, but, on analysis, appreciable quantities of the gold were detected even at a distance of more than 5 millimetres from the common surface, while within a distance of three-quarters of a millimetre from the surface gold had penetrated into the lead to the extent of 1 oz. 6 dwts. per ton, an amount which could have been profitably extracted.

Whether it is or is not possible to devise any other intelligible account of the cause of such phenomena, it is certain that a simple and adequate explanation is found in the hypothesis that matter consists of discrete parts in a state of motion, which can penetrate into the spaces between the corresponding parts of surrounding bodies.

The hypothesis thus framed is also the only one which affords a rational explanation of other simple and well-known facts. If matter is regarded as a continuous medium the phenomena of expansion are unintelligible. There is, apparently, no limit to the expansion of matter, or, to fix our attention on one kind of matter, let us say to the expansion of a gas; but it is inconceivable that a continuous material which fills or is present in every part of a given space could also be present in every part of a space a million times as great. Such a statement might be made of a mathematical abstraction; it cannot be true of any real substance or thing. If, however, matter consists of discrete particles, separated from each other either by empty space or by something different from themselves, we can at once understand that expansion and contraction may be nothing more than the mutual separation or approach of these particles.

Again, no clear mental picture can be formed of the phenomena of heat unless we suppose that heat is a mode of motion. In the words of Rumford, it is "extremely difficult, if not quite impossible, to form any distinct idea of anything capable of being excited and communicated in the manner the heat was excited and communicated in [his] experiment [on friction] except it be motion (*Phil. Trans.*, 1798, p. 99). And if heat be motion there can be no doubt that it is the fundamental particles of matter which are moving. For the motion is not visible, is not motion of the body as a whole, while diffusion, which is a movement of matter, goes on more quickly as the temperature rises, thereby proving that the internal motions have become more rapid, which is exactly the result which would follow if these were the movements which constitute sensible heat.

Combining, then, the phenomena of diffusion, expansion, and heat, it is not too much to say that no hypotheses which make them intelligible have ever been framed other than those which are at the basis of the atomic theory.

Many other considerations also point to the same conclusion. Many years ago Lord Kelvin gave independent arguments, based on the properties of gases, on the constitution of the surfaces of liquids, and on the electric properties of metals, all of which indicate that matter is, to use his own phrase, coarse-grained—that it is not identical in constitution throughout, but that adjacent minute parts are distinguishable from each other by being either of different natures or in different states.

And here it is necessary to insist that all these fundamental proofs are independent of the nature of the particles or granules into which matter must be divided.

The particles, for instance, need not be different in kind from the medium which surrounds and separates them. It would suffice if they were what may be called singular parts of the medium itself, differing from the rest only in some peculiar state of internal motion or of distortion, or by being in some other way earmarked as distinct individuals. The view that the constitution of matter is atomic may and does receive support from theories in which definite assumptions are made as to the constitution of the atoms; but when, as is often the case, these assumptions introduce new and more recondite difficulties, it must be remembered that the fundamental hypothesis —that matter consists of discrete parts, capable of independent motions—is forced upon us by facts and arguments

which are altogether independent of what the nature and properties of these separate parts may be.

As a matter of history the two theories, which are not by any means mutually exclusive, that atoms are particles which can be treated as distinct in kind from the medium which surrounds them, and that they are parts of that medium existing in a special state, have both played a large part in the theoretical development of the atomic hypothesis. The atoms of Waterston, Clausius, and Maxwell were particles. The vortex-atoms of Lord Kelvin, and the strain atoms (if I may call them so) suggested by Mr. Larmor, are states of a primary medium which constitutes a physical connection between them, and through which their mutual actions arise and are transmitted.

Properties of the Basis of Matter.

It is easy to show that, whichever alternative be adopted, we are dealing with something, whether we consider it under the guise of separate particles or of differentiated portions of the medium, which has properties different from those of matter in bulk.

For if the basis of matter had the same constitution as matter, the irregular heat movements could hardly be maintained either against the viscosity of the medium or the frittering away of energy of motion which would occur during the collisions between the particles. Thus, even in the case in which a hot body is prevented from losing heat to surrounding objects, its sensible heat should spontaneously decay by a process of self-cooling. No such phenomenon is known, and though on this, as on all other points, the limits of our knowledge are fixed by the uncertainty of experiment, we are compelled to admit that, to all appearance, the fundamental medium, if it exists, is unlike a material medium, in that it is non-viscous; and that the particles, if they exist, are so constituted that energy is not frittered away when they collide. In either case, we are dealing with something different from matter itself in the sense that, though it is the basis of matter, it is not identical in all its properties with matter.

The idea therefore that entities exist possessing properties different from those of matter in bulk is not introduced at the end of a long and recondite investigation to explain facts with which none but experts are acquainted. It is forced upon us at the very threshold of our study of Nature. Either the properties of matter in bulk cannot be referred to any simpler structure, or that simpler structure must have properties different from those of matter in bulk as we directly knew it—properties which can only be inferred from the results which they produce.

No *à priori* argument against the possibility of our discovering the existence of quasi-material substances, which are nevertheless different from matter, can prove the negative proposition that such substances cannot exist. It is not a self-evident truth that no substance other than ordinary matter can have an existence as real as that of matter itself. It is not axiomatic that matter cannot be composed of parts whose properties are different from those of the whole. To assert that even if such substances and such parts exist no evidence however cogent could convince us of their existence, is to beg the whole question at issue; to decide the cause before it has been heard.

We must therefore adhere to the standpoint adopted by most scientific men, viz., that the question of the existence of ultra-physical entities, such as atoms and the ether, is to be settled by the evidence, and must not be ruled out as inadmissible on *à priori* grounds.

On the other hand, it is impossible to deny that, if the mere entry on the search for the concealed causes of physical phenomena is not a trespass on ground we have no right to explore, it is at all events the beginning of a dangerous journey.

The wraiths of phlogiston, caloric, luminiferous corpuscles, and a crowd of other phantoms haunt the investigator, and as the grim host vanishes into nothingness he cannot but wonder if his own conceptions of atoms and of the ether

> "shall dissolve,
> And, like this insubstantial pageant faded,
> Leave not a wrack behind."

But though science, like Bunyan's hero, has sometimes had to pass through the "Valley of Humiliation," the spectres which meet it there are not really dangerous if they are boldly faced. The facts that mistakes have been made, that theories have been propounded, and for a time accepted, which later investigations have disproved, do not necessarily discredit the method adopted. In scientific theories, as in the world around us, there is a survival of the fittest, and Dr. James Ward's unsympathetic account of the blunders of those whose work, after all, has shed glory on the Nineteenth Century, might *mutatis mutandis* stand for a description of the history of the advance of civilisation. "The story of the progress so far," he tells us, "is briefly this: Divergence between theory and fact one part of the way, the wreckage of abandoned fictions for the rest, with an unattainable goal of phenomenal nihilism and ultra-physical mechanism beyond" (James Ward, "Naturalism and Agnosticism," vol. i., p. 153).

"The path of progress," says Professor Karl Pearson, "is strewn with the wreck of nations. Traces are everywhere to be seen of the hecatombs of inferior races, and of victims who found not the narrow way to the greater perfection. Yet these dead peoples are, in very truth, the stepping-stones on which mankind has arisen to the higher intellectual and deeper emotional life of to-day" (Karl Pearson, "National Life from the Standpoint of Science," p. 62).

It is only necessary to add that the progress of society is directed towards an unattainable goal of universal contentment, to make the parallel complete.

And so, in the one case as in the other, we may leave "the dead to bury their dead." The question before us is not whether we too may not be trusting to false ideas, erroneous experiments, evanescent theories. No doubt we are; but, without making an insolent claim to be better than our fathers, we may fairly contend that, amid much that is uncertain and temporary, some of the fundamental conceptions, some of the root-ideas of science, are so grounded on reason and fact that we cannot but regard them as an aspect of the very truth.

Enough has, perhaps, now been said on this point for my immediate purpose. The argument as to the constitution of matter could be developed further in the manner I have hitherto adopted, viz., by series of propositions, the proof of each of which is based upon a few crucial phenomena. In particular, if matter is divided into moving granules or particles, the phenomenon of cohesion proves that there must be mutual actions between them analogous to those which take place between large masses of matter, and which we ascribe to force, thereby indicating the regular, unvarying operation of active machinery which we have not yet the means of adequately understanding. For the moment, I do not wish to extend the line of reasoning that has been followed. My main object is to show that the notion of the existence of ultra-physical entities and the leading outlines of the atomic theory are forced upon us at the beginning of our study of Nature, not only by *à priori* considerations, but in the attempt to comprehend the results of even the simplest observation. These outlines cannot be effaced by the difficulties which undoubtedly arise in filling up the picture. The cogency of the proof that matter is coarse-grained is in no way affected by the fact that we may have grave doubts as to the nature of the granules. Nay, it is of the first importance to recognise that, though the fundamental assumptions of the atomic theory receive overwhelming support from a number of more detailed arguments, they are themselves almost of the nature of axioms, in that the simplest phenomena are unintelligible if they are abandoned.

The Range of the Atomic Theory.

It would be most unfair, however, to the atomic theory to represent it as depending on one line of reasoning only, or to treat its evidence as bounded by the very general propositions I have discussed.

It is true that as the range of the theory is extended the fundamental conception that matter is granular must be expanded and filled in by supplementary hypotheses as to the constitution of the granules. It may also be admitted that no complete or wholly satisfactory description of that constitution can as yet be given; that perfection has not yet been attained here or in any other branch of science; but the number of facts which can be accounted for by the theory is very large compared with the number of additional hypotheses which are introduced; and the cumulative weight of the additional evidence obtained by the study of details is such as to add greatly to the strength of the conviction that, in its leading outlines, the theory is true.

It was originally suggested by the facts of chemistry, and though, as we have seen, a school of chemists now thrusts it into the background, it is none the less true, in the words of Dr. Thorpe, that "every great advance in chemical knowledge during the last ninety years finds its interpretation in [Dalton's] theory" (Thorpe "Essays on Historical Chemistry," 1894, p. 368).

The principal mechanical and thermal properties of gases have been explained, and in large part discovered, by the aid of the atomic theory; and, though there are outstanding difficulties, they are, for the most part, related to the nature of the atoms and molecules, and do not affect the question as to whether they exist.

The fact that different kinds of light all travel at the same speed in interplanetary space, while they move at different rates in matter, is explained if matter is coarse-grained. But to attempt to sum up all this evidence would be to recite a text-book on physics. It must suffice to say that it is enormous in extent and varied in character, and that the atomic theory imparts a unity to all the physical sciences which has been attained in no other way.

I must, however, give a couple of instances of the wonderful success which has been achieved in the explanation of physical phenomena by the theory we are considering, and I select them because they are in harmony with the line of argument I have been pursuing.

When a piece of iron is magnetised its behaviour is different according as the magnetic force applied to it is weak, moderate, or strong. When a certain limit is passed the iron behaves as a non-magnetic substance to all further additions of magnetic force. With strong forces it does and with very weak forces it does not remain magnetised when the force ceases to act. Professor Ewing has imitated all the minute details of these complicated properties by an arrangement of small isolated compass needles to represent the molecules. It may fairly be said that as far as this particular set of phenomena is concerned a most instructive working model based on the molecular theory has not only been imagined but constructed.

The next illustration is no less striking. We may liken a crowd of molecules to a fog; but while the fog is admitted by everybody to be made up of separate globules of water, the critics of scientific method are sometimes apt to regard the molecules as mere fictions of the imagination. If, however, we could throw the molecules of a highly rarefied gas into such a state that vapour condensed on them, so that each became the centre of a water-drop, till the host of invisible molecules was, as it were, magnified by accretion into a visible mist, surely no stronger proof of their reality could be desired. Yet there is every reason to believe that something very like this has been accomplished by Mr. C. T. R. Wilson and Professor J. J. Thomson.

It is known that it is comparatively difficult to produce a fog in damp air if the mixture consists of air and water-vapour alone. The presence of particles of very fine dust facilitates the process. It is evident that the vapour condenses on the dust particles and that a nucleus of some kind is necessary on which each drop may form. But electrified particles also act as nuclei; for if a highly-charged body from which electricity is escaping be placed near a steam-jet, the steam condenses; and a cloud is also formed in dust-free air more easily than would otherwise be the case if electricity is discharged into it.

Again, according to accepted theory, when a current of electricity flows through a gas some of the atoms are divided into parts which carry positive and negative charges as they move in opposite directions, and unless this breaking-up occurs a gas does not conduct electricity. But a gas can be made a conductor merely by allowing the Röntgen rays or the radiation given off by uranium to fall upon it. A careful study of the facts shows that it is probable that some of the atoms have been broken up by the radiation, and that their oppositely electrified parts are scattered among their unaltered fellows. Such a gas is said to be ionised.

Thus by these two distinct lines of argument we come to the conclusions:—1st, That the presence of electrified particles promotes the formation of mist; and, 2nd, that in an ionised gas such electrified particles are provided by the breaking-up of atoms.

The two conclusions will mutually support each other if it can be shown that a mist is easily formed in ionised air. This was tested by Mr. Wilson, who showed that in such air mist is formed as though nuclei were present, and thus in the cloud we have visible evidence of the presence of the divided atoms. If then we cannot handle the individual molecules we have at least some reason to believe that a method is known of seizing individuals, or parts of individuals, which are in a special state, and of wrapping other matter round them till each one is the centre of a discrete particle of a visible fog.

I have purposely chosen this illustration, because the explanation is based on a theory—that of ionisation—which is at present subjected to hostile criticism. It assumes that an electrical current is nothing more than the movement of charges of electricity. But magnets placed near an electric current tend to set themselves at right-angles to its direction; a fact on which the construction of telegraphic instruments is based. Hence if the theory be true, a similar effect ought to be produced by a moving charge of electricity. This experiment was tried many years ago in the laboratory of Helmholtz by Rowland, who caused a charged disc to spin rapidly near a magnet. The result was in accord with the theory; the magnet moved as though acted upon by an electric current. Of late, however, M. Crémieu has investigated the matter afresh, and has obtained results which, according to his interpretation, were inconsistent with that of Rowland.

M. Crémieu's results are already the subject of controversy (see *Phil. Mag.*, July, 1901, p. 144; and *Johns Hopkins University Circulars*, xx., No. 152, May—June, 1901, p. 78), and are, I believe, likely to be discussed in the Section of Physics. This is not the occasion to enter upon a critical discussion of the question at issue, and I refer to it only to point out that though, if M. Crémieu's result were upheld, our views as to electricity would have to be modified, the foundations of the atomic theory would not be shaken.

It is, however, from the theory of ions that the most far-reaching speculations of science have recently received unexpected support. The dream that matter of all kinds will some day be proved to be fundamentally the same has survived many shocks. The opinion is consistent with the great generalisation that the properties of elements are a periodic function of their atomic weights. Sir Norman Lockyer has long been a prominent exponent of the view that the spectra of the stars indicate the reduction of our so-called elements to simpler forms, and now Professor J. J. Thomson believes that we can break off from an atom a part, the mass of which is not more than one-thousandth

of the whole, and that these corpuscles, as he has named them, are the carriers of the negative charge in an electric current. If atoms are thus complex, not only is the *a priori* probability increased that the different structures which we call elements may all be built of similar bricks, but the discovery by Lenard that the ease with which the corpuscles penetrate different bodies depends only on the density of the obstacles, and not on their chemical constitution, is held by Professor Thomson to be "a strong confirmation of the view that the atoms of the elementary substances are made up of simpler parts, all of which are alike."* On the present occasion, however, we are occupied rather with the foundations than with these ultimate ramifications of the atomic theory; and having shown how wide its range is, I must, to a certain extent, retrace my steps and return to the main line of my argument.

The Properties of Atoms and Molecules.

For if it be granted that the evidence that matter is coarse grained and is formed of separate atoms and molecules is too strong to be resisted, it may still be contended that we can know little or nothing of the sizes and properties of the molecules.

It must be admitted that though the fundamental postulates are always the same, different aspects of the theory, which have not in all cases been successfully combined, have to be developed when it is applied to different problems; but in spite of this there is little doubt that we have some fairly accurate knowledge of molecular motions and magnitudes.

If a liquid is stretched into a very thin film, such as a soap bubble, we should expect indications of a change in its properties when the thickness of the film is not a very large multiple of the average distance between two neighbouring molecules. In 1890 Sohncke (*Wied. Ann.*, 1890, xl., pp. 345—355), detected evidence of such a change in films of the average thickness of 106 millionths of a millimetre ($\mu\mu$), and quite recently Rudolph Weber found it in an oil-film when the thickness was 115 $\mu\mu$ (*Ann. der Phys.*, 1901, iv., pp. 706—721).

Taking the mean of these numbers and combining the results of different variants of the theory we may conclude that a film should become unstable, and tend to rupture spontaneously somewhere between the thicknesses of 110 and 55 $\mu\mu$, and Professor Reinold and I found by experiment that this instability is actually exhibited between the thicknesses of 96 and 45 $\mu\mu$ (*Phil. Trans.*, 1893, 184, pp. 505—529). There can therefore be little doubt that the first approach to molecular magnitudes is signalled when the thickness of a film is somewhat less than 100 $\mu\mu$, or 4 millionths of an inch.

Thirteen years ago I had the honour of laying before the Chemical Society a *résumé* of what was then known on these subjects (*Chem. Soc. Trans.*, March, 1888, liii., pp. 222—262), and I must refer to that lecture or to the most recent edition of O. E. Meyer's work on the kinetic theory of gases ("Kinetic Theory of Gases," O. E. Meyer, 1899, translated by R. E. Baynes), for the evidence that various independent lines of argument enable us to estimate quantities very much less than 4 millionths of an inch, which is perhaps from 500 to 1000 times greater than the magnitude which, in the present state of our knowledge, we can best describe as the diameter of a molecule.

Confining our attention, however, to the larger quantities, I will give one example to show how strong is the cumulative force of the evidence as to our knowledge of the magnitudes of molecular quantities.

We have every reason to believe that though the molecules in a gas frequently collide with each other, yet in the case of the more perfect gases the time occupied in collisions is small compared with that in which each molecule travels undisturbed by its fellows. The average distance travelled between two successive encounters is called the mean free path, and, for the reason just given, the question of the magnitude of this distance can be attacked without any precise knowledge of what a molecule is, or of what happens during an encounter.

Thus the mean free path can be determined, by the aid of the theory, either from the viscosity of the gas or from the thermal conductivity. Using figures given in the latest work on the subject (Meyer's "Kinetic Theory of Gases," see above), and dealing with one gas only, as a fair sample of the rest, the lengths of the mean free path of hydrogen as determined by these two independent methods differ only by about 3 per cent. Further, the mean of the values which I gave in the lecture already referred to differed only by about 6 per cent from the best modern result, so that no great change has been introduced during the last thirteen years.

It may, however, be argued that these concordant values are all obtained by means of the same theory, and that a common error may affect them all. In particular, some critics have of late been inclined to discredit the atomic theory by pointing out that the strong statements which have sometimes been made as to the equality, among themselves, of atoms or molecules of the same kind may not be justified, as the equality may be that of averages only, and be consistent with a considerable variation in the sizes of individuals.

Allowing this argument more weight than it perhaps deserves, it is easy to show that it cannot affect seriously our knowledge of the length of the mean free path.

Professor George Darwin (*Phil. Trans.*, 180), has handled the problem of a mixture of unequal spherical bodies in the particular case in which the sizes are distributed according to the law of errors, which would involve far greater inequalities than can occur among atoms. Without discussing the precise details of his problem it is sufficient to say that in the case considered by him the length of the mean free path is $\frac{1}{11}$ of what it would be if the particles were equal. Hence were the inequalities of atoms as great as in this extreme case, the reduction of the mean free path in hydrogen could only be from 185 to 110 $\mu\mu$; but they must be far less, and therefore the error, if any, due to this cause could not approach this amount. It is probably inappreciable.

Such examples might be multiplied, but the one I have selected is perhaps sufficient to illustrate my point, viz., that considerable and fairly accurate knowledge can be obtained as to molecular quantities by the aid of theories the details of which are provisional, and are admittedly capable of improvement.

Is the Model Unique?

But the argument that a correct result may sometimes be obtained by reasoning on imperfect hypotheses raises the question as to whether another danger may not be imminent. To be satisfactory our model of Nature must be unique, and it must be impossible to imagine any other which agrees equally well with the facts of experiment. If a large number of hypotheses could be framed with equal claims to validity, that fact would alone raise grave doubts as to whether it were possible to distinguish between the true and the false. Thus Professor Poincaré has shown that an infinite number of dynamical explanations can be found for any phenomenon which satisfies certain conditions. But though this consideration warns us against the too ready acceptance of explanations of isolated phenomena, it has no weight against a theory which embraces so vast a number of facts as those included by the atomic theory. It does not follow that, because a number of solutions are all formally dynamical, they are therefore all equally admissible. The pressure of a gas may be explained as the result of a shower of blows delivered by molecules, or by a repulsion between the various parts of a continuous medium. Both solutions are expressed in dynamical language; but one is, and the other is not, compatible with the observed phenomena of

* For the most recent account of this subject see an article on "Bodies smaller than Atoms," by Professor J. J. Thomson in the *Popular Science Monthly* (The Science Press), August, 1901.

expansion. The atomic theory must hold the field until another can be found which is not inferior as an explanation of the fundamental difficulties as to the constitution of matter, and is, at the same time, not less comprehensive.

On the whole, then, the question as to whether we are attempting to solve a problem which has an infinite number of solutions may be put aside until one solution has been found which is satisfactory in all its details. We are in a sufficient difficulty about that to make the rivalry of a second of the same type very improbable.

The Phenomena of Life.

But it may be asked—nay, it has been asked—may not the type of our theories be radically changed? If this question does not merely imply a certain distrust in our own powers of reasoning, it should be supported by some indication of the kind of change which is conceivable.

Perhaps the chief objection which can be brought against physical theories is that they deal only with the inanimate side of Nature, and largely ignore the phenomena of life. It is therefore in this direction, if in any, that a change of type may be expected. I do not propose to enter at length upon so difficult a question, but, however we may explain or explain away the characteristics of life, the argument for the truth of the atomic theory would only be affected if it could be shown that living matter does not possess the thermal and mechanical properties, to explain which the atomic theory has been framed. This is so notoriously not the case that there is the gravest doubt whether life can in any way interfere with the action within the organism of the laws of matter in bulk belonging to the domain of mechanics, physics, and chemistry.

Probably the most cautious opinion that could now be expressed on this question is that, in spite of some outstanding difficulties which have recently given rise to what is called Neovitalism, there is no conclusive evidence that living matter can suspend or modify any of the natural laws which would affect it if it were to cease to live. It is possible that though subject to these laws the organism while living may be able to employ, or even to direct, their action within itself for its own benefit, just as it unquestionably does make use of the processes of external nature for its own purposes; but if this be so, the seat of the controlling influence is so withdrawn from view that on the one hand its very existence may be denied, while, on the other hand, Professor Hæckel, following Vogt, has recently asserted that "matter and ether are not dead, and only moved by extrinsic force; but they are endowed with sensation and will; they experience an inclination for condensation, a dislike for strain; they strive after the one, and struggle against the other ("Riddle of the Universe," English translation, 1900, p. 380).

But neither unproved assertions of this kind nor the more refined attempts that have been made by others to bring the phenomena of life and of dead matter under a common formula touch the evidence for the atomic theory. The question as to whether matter consists of elements capable of independent motion is prior to, and independent of, the further questions as to what these elements are, and whether they are alive or dead.

The physicist, if he keeps to his business asserts, as the bases of the atomic theory, nothing more than that he who declines to admit that matter consists of separate moving parts must regard many of the simplest phenomena as irreconcilable and unintelligible, in spite of the fact that means of reconciling them are known to everybody, in spite of the fact that the reconciling theory gives a general correlation of an enormous number of phenomena in every branch of science, and that the outstanding difficulties are connected, not so much with the fundamental hypotheses that matter is composed of distinguishable entities which are capable of separate motions as with the much more difficult problem of what these entities are.

On these grounds the physicist may believe that, though he cannot handle or see them, the atoms and molecules are as real as the ice crystals in a cirrus cloud which he cannot reach; as real as the unseen members of a meteoric swarm whose death-glow is lost in the sunshine, or which sweep past us, unentangled, in the night.

If the confidence that his methods are weapons with which he can fight his way to the truth were taken from the scientific explorer, the paralysis which overcomes those who believe that they are engaged in a hopeless task would fall upon him.

Physiology has specially flourished since physiologists have believed that it is possible to master the physics and chemistry of the framework of living things, and since they have abandoned the attitude of those who placed in the foreground the doctrine of the vital force. To supporters of that doctrine the principle of life was not a hidden directing power which could perhaps whisper an order that the flood-gates of reservoirs of energy should now be opened and now closed, and could, at the most, work only under immutable conditions to which the living and the dead must alike submit. On the contrary, their vital force pervaded the organism in all its parts. It was an active and energetic opponent of the laws of physics and chemistry. It maintained its own existence not by obeying but by defying them; and though destined to be finally overcome in the separate campaigns of which each individual living creature is the scene, yet like some guerilla chieftain it was defeated here only to reappear there with unabated confidence and apparently undiminished force.

This attitude of mind checked the advance of knowledge. Difficulty could be evaded by a verbal formula of explanation which in fact explained nothing. If the mechanical, or physical, or chemical causes of a phenomenon did not lie obviously upon the surface, the investigator was tempted to forego the toil of searching for them below; it was easier to say that the vital force was the cause of the discrepancy, and that it was hopeless to attempt to account for the action of a principle which was incomprehensible in its nature.

For the physicist the danger is no less serious though it lies in a somewhat different direction. At present he is checked in his theories by the necessity of making them agree with a comparatively small number of fundamental hypotheses. If this check were removed his fancy might run riot in the wildest speculations, which would be held to be legitimate if only they led to formulæ in harmony with facts. But the very habit of regarding the end as everything, and the means by which it was attained as unimportant, would prevent the discovery of those fragments of truth which can only be uncovered by the painful process of trying to make inconsistent theories agree, and using all facts, however remote, as the tests of our central generalisation.

"Science," said Helmholtz, "Science, whose very object it is to comprehend Nature, must start with the assumption that Nature is comprehensible." And again:—"The first principle of the investigator of Nature is to assume that Nature is intelligible to us, since otherwise it would be foolish to attempt the investigation at all." These axioms do not assume that all the secrets of the universe will ultimately be laid bare, but that a search for them is hopeless if we undertake the quest with the conviction that it will be in vain. As applied to life they do not deny that in living matter something may be hidden which neither physics nor chemistry can explain, but they assert that the action of physical and chemical forces in living bodies can never be understood, if at every difficulty and at every check in our investigations we desist from further attempts in the belief that the laws of physics and chemistry have been interfered with by an incomprehensible vital force. As applied to physics and chemistry they do not mean that all the phenomena of life and death will ultimately be included in some simple and self-sufficing mechanical theory; they do mean that we are not to sit down contented with paradoxes such as that the same thing can fill

both a large space and a little one; that matter can act where it is not, and the like, if by some reasonable hypothesis, capable of being tested by experiment, we can avoid the acceptance of these absurdities. Something will have been gained if the more obvious difficulties are removed, even if we have to admit that in the background there is much that we cannot grasp.

The Limits of Physical Theories.

And this brings me to my last point. It is a mistake to treat physical theories in general, and the atomic theory in particular, as though they were parts of a scheme which has failed if it leaves anything unexplained, which must be carried on indefinitely on exactly the same principles, whether the ultimate results are, or are not, repugnant to common sense.

Physical theories begin at the surface with phenomena which directly affect our senses. When they are used in the attempt to penetrate deeper into the secrets of Nature it is more than probable that they will meet with insuperable barriers, but this fact does not demonstrate that the fundamental assumptions are false, and the question as to whether any particular obstacle will be for ever insuperable can rarely be answered with certainty.

Those who belittle the ideas which have of late governed the advance of scientific theory too often assume that there is no alternative between the opposing assertions that atoms and the ether are mere figments of the scientific imagination, or that, on the other hand, a mechanical theory of the atoms and of the ether, which is now confessedly imperfect, would, if it could be perfected, give us a full and adequate representation of the underlying realities.

For my own part I believe that there is a *via media*.

A man peering into a darkened room, and describing what he thinks he sees, may be right as to the general outline of the objects he discerns, wrong as to their nature and their precise forms. In his description fact and fancy may be blended, and it may be difficult to say where the one ends and the other begins; but even the fancies will not be worthless if they are based on a fragment of truth, which will prevent the explorer from walking into a looking-glass, or stumbling over the furniture. He who saw "men as trees walking" had at least a perception of the fundamental fact that something was in motion around him.

And so, at the beginning of the twentieth century, we are neither forced to abandon the claim to have penetrated below the surface of Nature, nor have we, with all our searching, torn the veil of mystery from the world around us.

The range of our speculations is limited both in space and time; in space, for we have no right to claim, as is sometimes done, a knowledge of the "infinite universe"; in time, for the cumulative effects of actions which might pass undetected in the short span of years of which we have knowledge, may, if continued long enough, modify our most profound generalisations. If some such theory as the vortex-atom theory were true, the faintest trace of viscosity in the primordial medium would ultimately destroy matter of every kind. It is thus a duty to state what we believe we know in the most cautious terms, but it is equally a duty not to yield to mere vague doubts as to whether we can know anything.

If no other conception of matter is possible than that it consists of distinct physical units—and no other conception has been formulated which does not blur what are otherwise clear and definite outlines—if it is certain, as it is, that vibrations travel through space which cannot be propagated by matter, the two foundations of physical theory are well and truly laid. It may be granted that we have not yet framed a consistent image either of the nature of the atoms or of the ether in which they exist; but I have tried to show that in spite of the tentative nature of some of our theories, in spite of many outstanding difficulties, the atomic theory unifies so many facts, simplifies so much that is complicated, that we have a right to insist—at all events till an equally intelligible rival hypothesis is produced—that the main structure of our theory is true; that atoms are not merely helps to puzzled mathematicians, but physical realities.

CONTRIBUTIONS TO THE SCIENCE OF THE NITROCELLULOSES.*

By G. LUNGE and J. BEBIE.

(Continued from p. 101).

D. *Solubility of the Nitrocelluloses in Ether-alcohol.*

The soluble nitration stages of cellulose play an important part in different industries, and octo- and enneanitrocellulose are more especially to be considered in this respect. But, as we have seen, these two nitration products do not indicate the limits of solubility; soluble products were obtained nearly down to heptanitrocellulose, and as far up as decanitrocellulose. These limiting cases are naturally less easily obtained than the middle products, as there is always the danger of forming traces of the lower or higher insoluble stages. Hence, if the nitrogen content does not come into consideration, and it is of sole importance to produce a completely soluble body, products with 174—184 c.c. NO are best adapted to the purpose. These nitrocelluloses are said to be insoluble in alcohol; those obtained by us were insoluble in 95 per cent alcohol, but were soluble in absolute alcohol, and, on the other hand, were insoluble in absolute ether. Hence, we might be inclined to think that, in the mixtures of ether and alcohol, the latter is the real solvent. But it appeared that the solubility in absolute alcohol did not run parallel with that in ether-alcohol; from enneanitrocellulose upwards the former diminishes rapidly.

The already mentioned solubility determinations refer to an ether-alcohol mixture of 3 : 1. A few more experiments were now started to determine to what extent this ratio may be varied without diminishing the solubility. (The product in question yielded 184 c.c. NO). With an ether-alcohol mixture of 6 : 1 complete solution was easily effected; with one of 9 : 1 the solubility began to become difficult, 95 per cent being still dissolved; in a mixture of 12 ether and 1 alcohol 92·1 per cent dissolved. With further diminution of the proportion of alcohol the solubility rapidly diminished; with the ratio 27 : 1 7·3 per cent was dissolved.

The converse was now investigated, viz., the extent to which the proportion of ether may be diminished. With an ether-alcohol mixture $\frac{1}{2}$: 1 complete solution easily resulted; with the ratio $\frac{1}{3}$: 1 solution became difficult, only 92 per cent dissolved after treating twice with the mixture; with the ratio $\frac{1}{7\frac{1}{2}}$: 1 it was remarkable that solution became again more easy, 96 per cent being dissolved after only one treatment; even with the mixture $\frac{1}{24}$: 1 95·6 per cent was dissolved. Hence, it is obvious that the alcohol plays the most important part in the mixture.

E. *Formula of Kisniemsky.*

A research of Kisniemsky appeared recently, in which an attempt was made to express in a simple ratio the relation between the composition of the nitration mixtures and the properties of the corresponding nitration products. The composition of the nitration mixture is brought into the form $1N_2O_5H_2O+aSO_3H_2O+cH_2O$, and the magnitude, $(1+a)-c=\mu$, is called the characteristic of the mixture. The nitration mixtures with $\mu > 0$ should produce highly nitrated, slightly soluble products; those, on the other hand, with $\mu < 0$ should give soluble products, and those in which μ rises but little above the value -1 products with the highest possible proportion of nitrogen.

* *Zeitschrift fur Angewandte Chemie*, 1901, Heft 20.

Our results were now reckoned in a similar manner, and, in general, they were in agreement with the above. But when μ nearly = 0 this value (as Kisniemsky himself has already observed) gives no result; between $-0{\cdot}3$ and $+0{\cdot}3$ there can be no reliable prediction of the properties. But this interval includes numerous important cases. In the others, also, the conclusion, especially as regards the proportion of nitrogen, is so indefinite that it forms no basis on which a nitration on the large scale could be conducted. Again, it is not to be inferred that the relation between the composition of the nitration mixture and the different properties of the corresponding nitrocelluloses can be expressed by so simple a formula.

F. *Influence of the amount of Nitrous Acid contained in the Nitric Acid on the Percentage of Nitrogen and the Gain of Nitrocellulose.*

The above mentioned nitrations were carried out with acid mixtures free from nitrous acid. As the amount of free nitrous acid in such mixtures is proportional to the degree of dilution, there is a considerable quantity of nitrous acid present with 10 per cent of water, while in concentrated acid mixtures this must all be converted into nitrosyl-sulphuric acid and nitric acid. Lunge and Weintraub have already proved that in this form it does not disturb the process of nitration; it still remained to investigate if this is also the case when the nitrous acid is retained as such in the nitration mixture.

The acid mixture used for this purpose had the following composition:—60·71 per cent H_2SO_4, 30·67 per cent HNO_3, 8·62 per cent H_2O. Hence the ratio of sulphuric acid to nitric acid was 1·98 : 1.

Equal portions of this mixture were treated with different quantities of nitrous acid. In this case also, up to a proportion of nitrous acid which would scarcely exist in practice, it is not possible to detect its influence either in regard to the percentage of nitrogen of the product or to the gain. This was of importance to us; for in the reverse case the results for obtaining higher nitration stages with dilute acid mixtures would have lost in practical significance.

Table XVII.

Expt.	C.c. NO per 1 grm.	N per cent.	Gain.	N_2O_4 per cent.
1.	216·15	13·55	174·53	0·13
2.	215·10	13·50	175·02	0·99
3.	216·30	13·56	173·98	0·84
4.	216·21	13·56	175·60	5·15

(To be continued).

THE ASSAYING OF COMPLEX GOLD ORES.*

By ERNEST A. SMITH, Assoc.R.S.M., F.C.S.,
late Assistant Instructor in Assaying, Royal School of Mines, London.

(Concluded from p. 100).

Auriferous Bismuth Ores.

Although not of frequent occurrence in nature, yet bismuth accompanies various ores of silver, and is also found occasionally associated with gold ores.

Bismuth is almost invariably found in nature in the metallic state; but occasionally it is met with as sulphide and as carbonate. It is also found in combination with tellurium associated with gold. Assays of auriferous bismuth ores are conducted like those of oxidised gold ores, but on account of the volatility of bismuth it is of importance that a readily fusible slag should be obtained, and for this purpose comparatively large quantities of sodium carbonate or of borax should be employed. When much bismuth is present the quantity of red-lead should be increased in order to effect its oxidation; a little nitre may also be added. Ores containing bismuth should not be roasted. A piece of iron should be added in the case of ores containing bismuthine or pyritic material.

It is not essential to pass the whole of the bismuth into the slag, but it is advisible to do so, otherwise it alloys with the lead, and although bismuth works on the cupel as satisfactorily as lead, yet the amount of gold and silver absorbed by the cupel and volatilised is greater when bismuth is present (E. A. Smith, *Journ. Chem. Soc.*, 1894, vol. lxv., p. 624). The fusion of the ore is conducted at a comparatively low temperature. After pouring the charge the mould should be left undisturbed until the slag is quite cold, as the effect of bismuth when combined with lead is to form more readily fusible alloys which remain in a molten condition for a much longer period than lead. If the proportion of bismuth does not exceed that of the lead the alloys are malleable, but the malleability is diminished with an increase of bismuth. The lead buttons obtained from the fusion, if inconveniently large, may be reduced in weight by scorification, but the temperature employed for this purpose should be low on account of the volatility of bismuth.

Scorification Process.

Although complex ores poor in gold are as a general rule better assayed by the fusion process in order that a comparatively large quantity of material may be operated upon, the scorification process is especially applicable to complex ores rich in gold and to concentrates. It may be remarked that in Germany and the United States the scorification process is in many cases preferred to the crucible process for all classes of ore, as the operations are easy to conduct, and very little variation is needed in the treatment of the different classes of ore. If the ore is poor, several assays (sometimes eight or ten) are made, and the resulting lead buttons scorified together. The small quantity of ore that can be treated constitutes the chief disadvantage of the process.

When the gold is distributed through the ore in comparatively large particles, the presence of one or two particles of metallic gold in an assay may cause the result to be erroneous. The larger charges operated upon in the crucible process are likely to give results which are nearer than those of the smaller charges to the average richness of the parcel of ore from which they are taken.

The quantity of material operated upon and of lead required for the scorification process varies with the nature of the substance to be assayed. As a general rule, not more than from 5 to 10 grms. of material are used, as these are the largest quantities which can conveniently be treated unless scorifiers of unusual size are employed. The weight of granulated lead necessary is generally from ten to fifteen times the weight of the material taken, but sometimes as much as twenty times its weight or even more is required. In the case of ores containing substances which yield lead, the quantity of granulated lead may be reduced to five times the weight of material taken for assay according to circumstances. The employment of insufficient lead is usually indicated by the presence of imperfectly fused particles in the slag or on the scorifier, notwithstanding the fact that the temperature has been sufficiently high. In order to facilitate the formation of a fluid slag a little borax is placed on the top of the contents of the scorifier, but care should be taken not to use a large quantity at the commencement of the operation, otherwise the surface of the molten lead becomes covered, and its oxidation is retarded. A convenient quantity to employ for 5 grms. of material is 0·1 grm., but this may be increased in special cases. If the slag appears pasty when the temperature is sufficiently high, more borax may be added, but it would be more satisfactory to repeat the assay with a larger proportion of lead. A small quantity (0·1 to 0·25 grm.) of powdered glass or very fine siliceous sand may be added with advantage for ores rich in copper. The following table gives the proportions of lead and of borax found by experience to be best adapted to the

* Abstract of Paper read before Institution of Mining and Metallurgy, May 15, 1901.

different classes of ore. The proportions are referred to one part of the material to be assayed :—

Character of material.	For one part of material take— Parts of granulated lead.	Parts of borax glass.
Antimonial	10 to 15	0·1 to 0·5
Arsenical		
Basic (FeO_3, Al_2O_3, CaO), &c.	10	0·25 to 1·0
Cupriferous	15 to 20	0·1 to 0·2
Fahlerz		
Galena and lead mineral ..	5 to 8	0·1
Pyritic (iron pyrites)	10 to 15	0·1 to 0·2
Siliceous	10	0 1
Zinc blende	10 to 15	0·1 to 0·2

The manipulation of the scorification process is too well known to need a detailed description here, but it may be pointed out that the losses frequently incurred are chiefly due to the employment of improper temperatures. The temperature, which is higher than that required for cupellation, should be well maintained during the process; if too low at first, gold and silver is liable to be retained in the slag. When the temperature has been too low, it is usually indicated by the occurrence of small white spots of lead sulphate on the surface of the slag after pouring. With very rich sulphides the results obtained are frequently much at variance with one another, which is probably due to the formation of oxysulphides (compounds of metallic oxides and sulphides), which remain in the slag, and retain considerable quantities of the precious metals. An excess of lead and a high temperature greatly help to prevent the formation of oxysulphides.

As a general rule, the loss of precious metals in the slag from scorification is small, but in the case of very rich ores it is always advisable to re-treat the slag. This may be done by re-scorifying in the same dish, or it may be fused in a crucible with suitable fluxes as previously described for slags from the crucible process.

Methods of "Concentration" for Poor Ores.

When assaying auriferous ores very poor in gold, the button of gold obtained from such quantities of ore (usually 50 grms.), as may be conveniently worked by the usual methods of assay is often so small as to require more than ordinary care in its manipulation.

In order to bring the button of gold within the scope of the balance and lessen the strain on the assayer's attention, larger charges of ore, of 100 or even 200 grms., are sometimes employed in the case of the poorest auriferous minerals. Large charges, however, are inconvenient, as they necessitate the use of large quantities of flux, and hence of very large crucibles. It is better, in the author's opinion, to make two independent fusions (or in exceptional cases three), each of 50 grms., and scorify the resulting lead buttons together, and repeat this process if necessary until the whole of the precious metals is concentrated in one button of lead of convenient size for cupellation. In the case of pyritic ores some assayers prefer to concentrate the precious metals in a regulus, which is subsequently treated for gold and silver.

Methods of concentration* for very poor ores have their advantages, but it must be admitted that they are usually tedious, laborious, and, to a considerable extent, uncertain. As the result of a series of experiments on the various methods of "concentration," the author has come to the conclusion that, although they may be advantageous in exceptional cases, as a general rule more satisfactory and trustworthy results are obtained by making independent fusions each of 50 grms. of ore, and concentrating the gold and silver in one button of lead as above indicated.

Summary.

The methods of assaying best adapted to the various complex ores enumerated may be summarised as follows:—

* Several methods of concentration are described in "Metallurgy of Gold," by T. K. Rose (see article on Assaying).

Basic Oxidised Ores.—Direct fusion, with special attention to the proportion of charcoal powder added to the charge, and the addition of metallic iron for ores containing a small percentage of pyritic material.

Pyritic Ores (mainly Iron Pyrites).—Roasting previous to fusion, and subsequent treatment as for basic ores. Fusion direct, with the addition of metallic iron, may be applied to ores containing 30 per cent or less of pyritic material. Oxidation with nitre can only be satisfactorily applied in cases where comparatively small quantities of pyritic material are present.

Arsenical Ores.—Preliminary roasting followed by fusion as for basic ores.

Antimonial Ores.—Generally oxidation with nitre.

Cupriferous Ores.—For ores rich in copper combined wet and dry methods. Ores comparatively poor in copper may be fused direct, or after a preliminary roasting, with the addition of suitable fluxes, due attention being given to the proportion of lead oxide added. The scorification process is convenient in cases where the ore is sufficiently rich in the precious metals to allow of this method being adopted.

Ores with Galena.—Fusion direct with addition of metallic iron. Roasting should not be attempted when much galena is present.

Ores with Blende.—Careful roasting and subsequent fusion as for basic ores, but with the addition of larger proportions of fluxes, which must be varied, according to the amount of zinc present.

Telluride Ores.—Fusion direct with very large proportions of lead oxide and ordinary fluxes. Scorification should on no account be employed.

Bismuth Ores.—Fusion direct as for basic ores. Scorification is not satisfactory when large quantities of bismuth are present.

Assay Office, Sheffield.

THE DISSOCIATING POWER OF DIFFERENT SOLVENTS.*

(A Summary).

By HARRY C. JONES.

(Continued from p. 108).

Organic Solvents (continued).

Formic and Acetic Acids.—Quite an elaborate investigation on the dissociating power of formic acid was carried out by Zanninovich-Tessarin (*Zeit. Phys. Chem.*, xix., 251). He used chiefly the freezing-point method, but also determined the conductivity of a few salts in this solvent. He measured the freezing-point lowering of formic acid produced by the following substances, at dilutions ranging from 0·34 to 3·4 normal (and in some cases at even greater concentration):—Potassium, sodium, ammonium, and lithium chlorides; potassium, sodium, and ammonium bromides; hydrochloric, acetic, and trichloracetic acids. A few of his results are given:—

Potassium chloride.		Sodium bromide.		Hydrochloric acid.	
Concent.	Diss.	Concent.	Diss.	Concent	Diss.
Normal.	Per cent.	Normal.	Per cent.	Normal.	Per cent.
0·341	74	1·522	51	1·82	0
1·055	62	2·509	54	2·20	0
2·263	63	4·995	60		

Formic acid is, thus, one of the strongest dissociating solvents next to water. The behaviour of hydrochloric acid in this solvent is very surprising. It not only shows no dissociation in formic acid, but the molecules are actually polymerised. The conductivities of potassium and sodium chlorides in formic acid were found to be very

* *American Chemical Journal*, xxv., No. 3.

large, and hydrochloric acid showed considerable conductivity in this solvent, although the freezing-point lowering indicated polymerisation instead of dissociation. This may be due to the fact that while most of the molecules were polymerised into very large complexes, some few were dissociated into ions which carried the current.

Zanninovich-Tessarin (*Zeit. Phys. Chem.*, xix., 255), also determined the freezing-point lowering of acetic acid produced by sodium bromide and lithium chloride. The former gave normal values, indicating no dissociation, while the latter showed very marked polymerisation.

The conductivity of sulphuric acid in acetic acid has been measured by Jones (*Amer. Chem. Journ.*, xvi., 13), who found that the molecular conductivity, which was small at all dilutions, increased with the dilution to a certain point ($v=3$), and then decreased with further increase in the dilution of the solution. This is somewhat analogous to the result obtained by Kablukoff (*Zeit. Phys. Chem.*, iv., 431), for hydrochloric acid in ether and in isoamyl alcohol.

The Nitriles.—The conductivities of mercuric chloride, sodium bromide, cadmium bromide and iodide, ammonium sulphocyanate and silver nitrate, in propionitrile, were determined by Dutoit and Aston (*Comptes Rendus*, cxxv., 240). This investigation was extended by Dutoit and Friderich (*Bull. Soc. Chim.*, [3], xix., 321), to solutions in acetonitrile and butyronitrile. The dissociating power of these three related substances can be seen from the following figures :—

	Silver nitrate.	Acetonitrile.	Propionitrile.	Butyronitrile.
		μ_v.	μ_v.	μ_v.
v =	8	54·5	14·21	—
v =	128	118·3	34·42	23·8
v =	256	131·5	38·86	35·5

The dissociating power is obviously greater in the first members of the series of nitriles, and becomes less as we ascend the series.

(To be continued).

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Cerite.—Can any reader inform me how to estimate quantitatively the Ce, La, Di, Nb, and Ta in cerite, or tell me where I could find this information?—Cerite.

Iron-mould Spots.—Can any reader give me a recipe whereby iron-mould spots and similar stains in old water-colour drawings can be removed without doing injury to the paper?—H.

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THE CHEMICAL NEWS.

Vol. LXXXIV., No. 2182.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

Glasgow, 1901.

By PERCY F. FRANKLAND, Ph.D., M.Sc., F.R.S., Professor of Chemistry in the University of Birmingham. President of the Section.

The Position of British Chemistry at the Dawn of the Twentieth Century.

Two circumstances unite in rendering this year especially appropriate for the survey and valuation of all departments of British life and organisation—the dawn of a new century, the close of the Victorian era. It is a moment when not only the nation as a whole, but every group of persons drawn together by whatever bond, and indeed each individual for himself, must involuntarily ask the question—Are we progressing or receding, or are we standing still? Upon us, then, who are bound together by the common interest which we have in that science to which this Section is devoted, there forces itself the question—What is the position of British Chemistry at the present moment, how does this present bear comparison with the past, and what are the prospects for the future?

To bring before you some considerations with respect to the answer which should be given to this question, or rather series of questions, will be my endeavour in responding to the honour which has been conferred on me of inaugurating the work of our Section at this Meeting of the Association.

It is with no light heart that I undertake this task, for there are present here to-day those whose much longer experience and far more intimate connection with the progress of our science render it presumption on my part to address them on this subject at all.

It is well known that the history of British Chemistry, as indeed that of British Science in general, is a very remarkable one; it is almost entirely made up of achievements which are the result of private initiative; and the persons who have taken part in the making of this history have, with some notable exceptions, not been servants of the State, and have thus differed from the makers of scientific history in almost every other country in the world. Thus the opportunities for the investigations which are recorded in the *Transactions* of our Chemical Society have, for the most part, not been provided out of the public purse, but by private individuals or by institutions which have been created by private benefaction.

This unique condition of things is well illustrated by taking up a volume of the Chemical Society's *Journal* and glancing at the table of contents.

Thus in the volume for 1881, taken at random, we find that, out of the seventy-five original communications which it contains, only thirteen emanate from Government laboratories, whilst what will surely not a little surprise the scientific historian of some centuries hence, is the circumstance that there are only four communications from the so-called "ancient seats of learning" of the United Kingdom, no fewer than three of which are by one and the same investigator. Again, most noteworthy is the fact that as many as five contributions are from distinguished amateurs. We have been told, on what many persons regard as high authority, that England is suffering from amateurism in all departments of life; and however true this may be as a general proposition, the amateurs of British Science, like Gladstone, Schunck, and Perkin amongst living chemists, are assuredly some of the most valued possessions of this country.

On looking back a quarter of a century into the past, it is at once apparent how greatly during that short period of time—less than a generation of men—have the opportunities for higher chemical training been extended and multiplied in our midst. I think I shall not be far wrong in saying that until twenty-five years ago practically the only public laboratories in which the higher study of chemistry could be pursued were those of the Royal College of Chemistry, the Royal Institution, of University and King's Colleges, London, the University laboratories of England, Scotland, and Ireland, as well as those of the Queen's Colleges and of the Royal College of Science in the sister island; to which must be added the laboratories of two institutions of a somewhat different type, viz., Owens College, Manchester, and Anderson's College, in this great city of the north. It is the rapid multiplication of institutions of the Owens College type that constitutes probably the most important feature in the higher intellectual development of the population of this country during the past quarter of a century; indeed, it may very possibly be found in the future that this constitutes the most striking landmark in the history of British intellectual progress during recent times. A glance at the following table will show the remarkably rapid growth of these institutions during the last quarter of the Nineteenth Century:—

Opening of University Colleges.

University College, London	1828
King's College, London	1831
Owens College, Manchester	1851
Durham College of Science, Newcastle ..	1871
University College, Aberystwyth	1872
Yorkshire College, Leeds	1875
University College, Bristol	1876
University College, Nottingham	1877
Firth College, Sheffield	1879
Mason College, Birmingham	1880
University College, Liverpool	1882
University College, Dundee	1882
University College, Cardiff	1883
University College, Bangor	1884
Finsbury Technical College } City Guilds.	1883
Central Institution .. .. }	1885

Thus the opening of the greater number of these institutions falls within the decade 1875—1884.

The benefits arising from the creation of these numerous institutions have not, however, been by any means limited to those persons who have actually taken advantage of their instruction, for their existence has stimulated the establishment of many other institutions, some of which, like the two colleges founded and maintained out of the resources of the City and Guilds of London, although more limited in their scope, afford equal or even greater opportunities for higher scientific training in the particular branches which are represented.

The foundation of these University Colleges and of other institutions for higher education by private initiative, and without a particle of assistance from the public exchequer, is quite in keeping with the history of a country in which it is recognised that the Government does not lead, but only follows where it is drawn or propelled.

It would certainly be anticipated that such a large addition to the machinery for higher scientific training as is represented by the creation of these numerous local colleges during the past twenty-five years would have had a marked influence on the output of scientific discovery in this country. We will endeavour to ascertain whether such a result is discernible in the case of chemical science. Turning to the *Transactions of the Chemical Society*, I have compiled the following table in the hope of obtaining some information on this point:—

Original Communications in the Transactions of the Chemical Society.

1849 ..	29	1866 ..	47	1883 ..	63
1850 ..	33	1867 ..	49	1884 ..	57
1851 ..	33	1868 ..	47	1885 ..	85
1852 ..	28	1869 ..	37	1886 ..	85
1853 ..	22	1870 ..	38	1887 ..	88
1854 ..	23	1871 ..	28	1888 ..	75
1855 ..	30	1872 ..	32	1889 ..	71
1856 ..	14	1873 ..	46	1890 ..	71
1857 ..	14	1874 ..	49	1891 ..	95
1858 ..	30	1875 ..	49	1892 ..	90
1859 ..	21	1876 ..	54	1893 ..	104
1860 ..	25	1877 ..	58	1894 ..	83
1861 ..	32	1878 ..	61	1895 ..	116
1862 ..	81	1879 ..	84	1896 ..	117
1863 ..	51	1880 ..	75	1897 ..	114
1864 ..	54	1881 ..	75	1898 ..	102
1865 ..	49	1882 ..	65	1899 ..	120
				1900 ..	127

(The information furnished by these figures was presented in a graphic form by means of a diagram).

The activity displayed in chemical research, as measured by the number of original communications to the Chemical Society, is, however, best followed by a consideration of the aggregate number of papers contributed during the three following decades:—

Decade.	Total number of papers in *Transactions of Chemical Society.*
1855—1864	352
1865—1874	422
1875—1884	641
1885—1894	847

From these figures it is manifest, even without the application of any of those mathematical processes in which modern chemists are becoming so expert, that the most remarkable increase in the number of original investigations is indeed coincident with that decade, 1875—1884, in which the great majority of the institutions to which I have referred began to throw their prismatic rays of knowledge on many thousands who until then were sitting in shadow or even in darkness.

That these new institutions should have so immediately borne fruit in the manner I have indicated cannot fail to be surprising to those who have been associated with the early years of almost any of these colleges, for when a faithful record of the experiences of their first professors is written the extraordinary obstacles which these pioneers had to encounter, and which in so many cases they successfully overcame, should afford material for a most remarkable, instructive, and even amusing volume. The worthy founders and their executors or trustees appear in general to have supposed that it was only necessary to provide a spacious building, and then appoint a staff of professors who were to do the rest, whilst the necessity of funds for annual upkeep, for libraries, and for assistants was almost overlooked.

It has, indeed, been learnt by bitter experience that the cost of efficiently maintaining institutions of this most ambitious character is enormously greater than was supposed in this country twenty-five years ago, and that founding a college, far from resembling the inauguration of a remunerative business, is very like entrance into the bond of matrimony, with its attendant annually increasing demand upon the pecuniary resources of the paterfamilias.

It would not, indeed, be surprising if some of these modern colleges had been long debarred from contributing directly to the progress of scientific investigation in this country, for this was often assuredly considered amongst the least of the many arduous duties imposed upon their first professors. Ascertained capacity to enrich science was in some cases almost a presumptive disqualification for their chairs, or at any rate took a back seat beside enthusiasm for evening classes and faith in the efficacy of that mysterious panacea "technical instruction." It is indeed lamentable to think of the valuable years of productive work lost to the country through so much of the energy of these early professors having been sacrificed to these veritable fetishes of our would-be educational reformers.

Notwithstanding the unfavourable conditions under which most of these university colleges had in the first instance to carry on work, it was not long before they showed that they were to become, even during the tenure of office of their first professors, important centres for the prosecution of research—at least as far as chemical science was concerned. Owens College had indeed already led the way in this matter before the period with which I am more especially concerned to-day, for there the first professor of chemistry had pursued his memorable investigations on the organo-metallic compounds, and had, within the first five years after the foundation of the College, enunciated that generalisation which was subsequently extended into the *law of valency*; whilst under his successors, Sir Henry Roscoe, Schorlemmer, Harold Dixon, and Perkin, jun., the Owens College has become perhaps the largest and best equipped school of scientific chemistry in the British Isles.

From the Yorkshire College, Leeds, opened in 1875, there proceeded immediately in rapid succession that whole series of careful investigations relating more especially to specific volume and other physical constants which we associate with its first chemical professor, Thorpe, and his coadjutors.

In the west of England, where the University College of Bristol was opened in 1876, the chair of chemistry was first occupied by the man who has so recently once more proved to the world that there are discoveries made in these islands which for striking originality and independence are unsurpassed and hardly equalled elsewhere. It was during his tenure of the chair at Bristol that Ramsay, assisted by his able fellow-worker and successor Sydney Young, carried out those important and most laborious investigations on vapour pressure and the thermal properties of liquids which not only displayed his extraordinary fertility and resource as an experimenter, but also revealed that exceptional freshness of mind which has enabled him to discern new methods of attacking problems that have already engaged the attention of many able men before him.

Turning from the west of England to the Midlands, where, in 1880, there was founded, through the private munificence of the late Sir Josiah Mason, a college bearing his name, which, before even attaining its majority, was transformed at the psychological moment, as by the wand of the magician, into the University of Birmingham. The first professor of chemistry at the Mason College, my distinguished predecessor Tilden, soon made opportunity there to continue those early researches on the terpenes with which his name will always be associated. We find him also further elaborating the important uses as a reagent of nitrosyl chloride, which he had a number of years previously shown how to prepare in a state of purity, and which has played a somewhat similar part in the exploration of the terpene hydrocarbons that phenylhydrazine has done in the elucidation of the sugar group. In addition to these investigations, we find Tilden at Birmingham also turning his attention to some of the phenomena attending the solution of salts. The younger men attached to the Mason College also found there the opportunity of enriching chemical science with the results of notable investigations; for do we not all remember Thomas Turner's valuable contributions to our knowledge of the influence of chemical composition on the physical and mechanical properties of cast-iron? Whilst early amongst those detailed investigations on the phenomena of solution, which in recent years have had such far-reaching effects on the development of our science, must be mentioned Dr. Nicol's experiments on the volume changes attending the mixture of salt solutions, and on the molecular volume, the boiling-point, and expansion of such solutions.

In the bleak north east of our island, at Dundee, where a college was founded in 1882 with an extremely handsome endowment by members of the Baxter family, the first professor of chemistry, Carnelley, fired by that restless and almost perfervid energy which doubtless hastened his untimely end, soon found opportunity to interrogate Nature in various directions, notwithstanding the arduous teaching duties which his insatiable love of work had imposed upon himself. Thus, already in 1884, we find him, in his quest for material which should throw light on the periodic relationship of the elements, continuing his laborious work on melting-points and publishing those two ponderous quarto volumes in which every known melting-point was recorded, and forming truly one of the most remarkable compilations ever attempted in our science. Of these volumes he might indeed have said, "Exegi monumentum ære perennius," for they will assuredly prove a record of the boundless energy which characterised the man, more imperishable even than the memorial tablet erected by his admiring students and friends in the entrance hall of the Dundee laboratory, which he built and loved so well.

Yet another chemist, whose untimely death we have had to lament during the past twenty years, laboured with marked zeal in one of these new colleges, for it was at Aberystwyth that Humpidge, regardless of his delicate health, and in spite of the altogether unreasonable burden of teaching duties imposed upon him by the terms of his appointment, contributed to our knowledge of the atomic weight of beryllium, and participated in establishing the position occupied by that metal in the natural classification of the elements.

Time does not permit me to further dilate upon the great activity displayed by many of the first occupants of the chairs of chemistry in these provincial University Colleges. It is also unnecessary for me to do more than remind you of the work accomplished by the two Colleges of the City and Guilds of London, the chemical laboratories of which have from their very inception been under the stimulating influences of Dr. Armstrong and Professor Meldola, foci of research from which a number of young chemists of distinction have already emanated.

In recent years we have witnessed the genesis of another class of institution, less ambitious in their aspirations than the University Colleges, but indirectly also of much importance in their bearing upon the nurture of scientific chemistry in this country. I refer to the so-called Polytechnics which have sprung up in several parts of the Metropolis, and to some other institutions of similar scope in different parts of the country. If research in the University Colleges has been the product of their professors rather than of the environment which they afford, assuredly this is even far more so in the case of these Polytechnics, which are primarily evening schools for the benefit of those who have other occupations during the day. That the young lecturers on chemistry at these places should find time and opportunity for original research, and that sometimes of a very high order, is indeed a brilliant testimonial to their indomitable energy, and resourcefulness. Overburdened with large classes until late hours at night, often in those remote and hideous parts of London which suggest to most of us only Slumland, and the philanthropic efforts of Toynbee Hall, or of Dr. Barnardo, these young chemists awake in the morning only to return as rapidly as possible to those laboratories which exercise on them a fascination as subtle and magnetic as that which draws the commonplace Englishman to the golf-links, the cricket-field, or the racecourse. It was in the laboratory of such a technical school, the Heriot Watt College, at Edinburgh, that my distinguished predecessor in this chair, my friend Professor Perkin, created his opportunities for devising and carrying out those now classical methods of building up carbon rings which are the admiration of all organic chemists throughout the world; methods which he has recently brought to such a pitch of perfection that he is not only able to forge these rings in great variety, but to "bridge" them with links of carbon atoms. It was at the Heriot Watt College also that his work on berberin was performed, and it was here that he contracted that fertile alliance with Dr. Kipping, his able coadjutor in so many valuable investigations.

At the London Polytechnics, again, more recently, we have had similar examples of fertility, for are we not all familar with the masterly work of Mr. W. J. Pope, who by his investigations at the Goldsmiths' Institute has extended our knowledge of asymmetric atoms, and has shown that optical activity, which hitherto had only been associated with carbon, and somewhat doubtfully with nitrogen, can certainly be produced, not only by asymmetric pentad nitrogen, but also by tetravalent tin and sulphur? Dr. Hewitt, again, whom I am proud to number among my former students, has shown that the laboratory of the People's Palace, Mile End, may be made a centre in which abstruse investigations on the aromatic compounds can be carried on.

There is, however, perhaps nothing which testifies more strongly to the zeal for original investigation amongst British chemists than the manner in which some of the science masters at our schools have participitated in the advancement of chemical knowledge. Some of these schools have, indeed, from time to time secured the services of men whose names are indelibly engraved on the records of scientific chemistry, and it is from the laboratories of these schools that in some cases perhaps their best work has emanated. Of the chemical investigators who have laboured in school laboratories there occur to me, amongst the living, Debus and Clowes at Queenwood, Tilden and Shenstone at Clifton, Purdie at Newcastle-under-Lyme, Brereton Baker at Dulwich, Charles Baker at Shrewsbury. To these names might be added many more; indeed, an examination of the list of Fellows of the Chemical Society shows at what a number of schools throughout the country the chemical teaching is now imparted by men who have themselves advanced the science which they profess.

From the conspicuous instances which I have brought before you—and they might, did time allow, be greatly multiplied—it must be obvious that if a chemist only possesses the necessary enthusiasm and qualifications he will, no matter how inauspicious his surroundings, succeed in doing something to extend the boundaries of his science, and I think I may go further and say without fear of contradiction that in this devotion to research the chemist in this country usually throws into the shade the representatives of other branches of science. How is this pre-eminent zeal of the British chemist to be explained? I believe that there are two principal causes in operation which have brought about this result. Firstly, the great majority of the higher chemical teachers in this country have been trained in Germany, or have been trained by men who were themselves trained there; and secondly, they have only in exceptional cases been educated at the ancient seats of learning. Their inspiration and enthusiasm are almost invariably directly or indirectly traceable to a German origin, and this fire is kept alive by their remaining in constant touch with German chemical literature.

It is being continually impressed upon us in the newspapers, and dinned into our ears from every platform, that it is imperative for this country to approximate more to German ideas and methods, and in general to cast away our insular prejudices, obstinacy, and self-satisfaction. We chemists have already done these things; we have emancipated ourselves from the mischievous illusions which have a tendency to thrive in a country enjoying an isolated geographical position. For, during the last half century the academic springs of Germany have been visited by a stream of young English chemists, a stream which, for the perennial regularity of its flow, reminds one indeed of the pilgrimage made by our fashionable invalids to the same country in the hope of correcting the

effects of high living by the waters of Homburg, Kissingen, and Wiesbaden. There must indeed be few chemists who return from the German temples of science without bringing back at least a spark of the sacred fire to be kindled on an altar at home; and although at times it may be stifled by the island fog, or even burn low through the scarcity of fuel, it generally smoulders long before going out altogether.

The chemist, again, is generally, as I have said, unfettered by an English university record; he stands or falls by the work of his life, and not, as so many others do, by the reputation which they have made in three short years of adolescence at one of the ancient seats of learning.

The spirit of research, which was formerly but a sporadic manifestation within the walls of these venerable institutions, has, however, now become endemic there also, and for a number of years past chemical literature has received a continuous stream of original communications from Oxford and Cambridge, as well as from the Universities of Scotland and Ireland. Instead of those occasional contributions which were customary in the past, we have now evidence that these centres in several cases yield to none in the energy and success with which chemical investigation is being pursued, and that the work of the chemical staff is being shared in by advanced pupils trained at these universities themselves. In this connection it is quite unnecessary for me to remind you of the contributions to British chemistry within recent years by Crum Brown and his pupils at Edinburgh, by Japp at Aberdeen, by Purdie and James Walker at the duplex university now working so harmoniously north and south of the Tay, by Emerson Reynolds at Dublin, and by Harcourt and Harold Dixon, Liveing and Dewar, Ruhemann, Heycock and Neville, Fenton, Sell, Marsh, and others, who have brought our science into such living prominence on the banks of the Cam and the Isis.

It is, however, not at home only that British chemists have displayed their devotion to research, for with the world-wide relations of the empire it has naturally fallen to the lot of some of our number to carry the science to the uttermost parts of the earth, but it is surely a matter of which we may be justly proud that some of these missionaries, like Mallet, Liversidge, Pedler, and Rennie, have in these distant lands carried out a number of most important scientific investigations; whilst to one of them, Dr. Divers, belongs the great distinction, not only of having carried chemistry to the Far East, but of having reared a most active school of chemical research in that fascinating island empire of the rising sun and the chrysanthemum which has won the unfeigned admiration of the West.

The annals of British chemistry are, however, by no means an exclusive record of the exploits of those engaged in the teaching of our science. I have already referred to the importance of the contributions made by men of leisure, but an equally noteworthy feature of British chemistry is that its progress has been so often furthered by men who have snatched the time for investigation out of a busy professional or industrial life. Belonging to this category the names of a long line of distinguished chemists of our own time suggest themselves:—Warren de la Rue, Hugo Müller, Sir John Lawes, Sir William Crookes, Sir William Abney, Peter Griess, Newlands, O'Sullivan, Horace and Adrian Brown, Harris Morris, Cross and Bevan. To this group of chemists belongs also Dr. Ludwig Mond, whose technical researches have been of such great value to industrial chemistry, whilst his devotion to the pure science is attested by his interesting discovery and investigation of the metallic carbonyl compounds, and by his conception and munificent endowment of the Davy-Faraday Laboratory, in which such unique opportunities for research have been provided by him.

This would appear to be the most fitting moment also to refer to certain other institutions intended for purposes of research which have been established during the past twenty-five years. Of these the first is the Rothamsted Laboratory, so celebrated during the last half-century for the memorable investigations of Lawes, Gilbert, Pugh, and Warington, but which has more recently, through the generosity of the late Sir John Lawes, been rendered a permanent home for the elucidation of agricultural problems both by laboratory experiments and by trials in the field. Secondly, there is the Research Laboratory which the Pharmaceutical Society has established with the view of raising to a higher level the chemical education of its most promising future members. This laboratory has furnished the opportunity for the valuable investigations of its first director, Professor Dunstan, and of his successor, Dr. Collie. Still more recently a chemical research laboratory has been established in the Imperial Institute. That noble building has within the last few years undergone a process of transverse sub-division, one-half having assumed an independent existence as the nucleus of that still crystallising body, the University of London; whilst in the remaining half the work of the Institute is now carried on in such silence that we have almost forgotten its existence. For where is the florid music with which on summer nights the air of South Kensington was wont to reverberate? Gone. Gone also are the tea-tables, the gardens with their million fairy lights, and the promenading crowds in gay attire. But if the Institute, founded by public subscription to watch over and advance the prosperity of the British dominions, has been impoverished by the discontinuance of these revels, it has become enriched and has gained in dignity by the creation within its walls of a Research Laboratory in which Professor Dunstan and his assistants are busily investigating the chemical nature of numerous interesting products obtained from all parts of Greater Britain.

There can, in my opinion, be no doubt that this much extended cultivation of scientific chemistry in this country, which is such a noticeable feature of the concluding years of the Nineteenth Century, has been greatly assisted by a most fortunate, and more or less accidental, circumstance, without which the energy and enthusiasm of our chemical teachers would have been seriously restricted in their influence. I refer to the very substantial surplus, producing an income of £6000 to £7000 a year, of which the Commissioners of the 1851 Exhibition found themselves possessed, and its utilisation on the advice of the late Lord Playfair for the purpose of the Research Scholarships which have for some ten years past been so highly prized by all the educational institutions permitted to participate in them. The good wrought by these scholarships has been very far-reaching, and it would be difficult to praise too highly the wisdom displayed by the Commissioners in drawing up the conditions on which they are awarded. Firstly, by not limiting them to any one science, they have stimulated a wholesome rivalry between departments to bring on their promising students to the level of scientific investigation. Secondly, they have compelled the governing bodies of educational institutions to recognise and make provision for research as part of the regular programme of these places. Thirdly, they have encouraged talented students to devote an additional year, or even more, to their education in the hope of securing one of these prizes; and these students have thus provided their teachers with the *personnel* necessary for carrying on scientific work. Fourthly, the scholars themselves have had the inestimable advantage of extending their horizon, and of coming in contact with other teachers, other schools of thought, and other views of life. Fifthly, these scholars on their return, and before they have obtained definite employment, are welcomed as supernumeraries in English colleges, where they have an opportunity of continuing their researches, and where they assist in imbuing the students with the spirit which they have themselves imbibed. Lastly, these and other scholarships of a similar character are providing the country with a body of highly trained men whose value to the nation is annually becoming more appreciated, and whose work will con-

tinue to bear fruit directly or indirectly for an indefinite period of time. These Exhibition scholarships have now been awarded since 1891, and already no fewer than sixty-five chemists, including three women, have enjoyed the enormous privilege of extending their education for a period of two, and in special cases even three, years under the most favourable surroundings.

Bearing in mind the rooted objection which pervades the people of this country to expend any public money on higher education, it is marvellous that it should have been possible to employ this fund, which after all is of a quasi-public character, for what may be described as educational use at a high potential, instead of its being dissipated in the manner so dear to Englishmen, by benefiting to an infinitesimal extent a much larger number of persons. Indeed, but for the vertebrate character of the Commissioners in 1877, the fund would have been thus fritted away, for in that year they were waited upon by a deputation of influential persons who urged that the money should be distributed in grants to provincial museums. Had that been done what would have been the result? The masses would have had a few more glass cases to gaze at on wet days and bank holidays!

There can, I think, be little doubt that in this matter of the allocation of funds intended for the public good we have reached a turning-point in the road which we have been so long pursuing. Until recently it has been the feeling of a very powerful majority in this country that public money should only be spent in such a way as to directly benefit very large numbers; and in the case of educational funds, therefore, it was only their utilisation for the benefit of the masses that could be entertained. Now, whilst it is indubitable that the improvement of our primary education was for many years a crying necessity, it has long been obvious to a minority that this policy is systematically starving that higher education in which we are lagging more and more behind those other countries in which greater elasticity prevails, and in which the immediate and obvious wants of the community receive prompt attention without regard to the traditions and doctrinaire principles of a past generation. In the matter of higher scientific education, at any rate, it is becoming more and more widely recognised that its starvation through attention being exclusively directed to the low-level education of the masses is defeating the very ends which this policy has in view. Indeed, some practical men, and even a few statesmen, realise that the many are beginning to suffer from the results which this policy has had on our manufactures and commerce, without which the multitude can have no existence at all.

The more than princely patronage of higher education by that Scotsman who has not forgotten the land of his birth during fifty years spent in a country which has afforded the necessary scope for his genius and energies, illustrates the change in the wind of opinion amongst practical men; for Mr. Andrew Carnegie's handsome contribution to the funds of the University of Birmingham, and his endowment of the universities of Scotland on a scale which is altogether without precedent, clearly show which, in his opinion, are the rungs in the educational ladder of this country that require strengthening in the interest of those very masses which it is his earnest desire to benefit. The still more recent response of the City Council of Birmingham to Mr. Chamberlain's suggestion that a rate should be levied in aid of the university of that city is further evidence that Mr. Carnegie's practically expressed opinion is shared by the enlightened rulers of that great municipality to which I have the privilege of belonging.

These, ladies and gentlemen, are, I believe, no mere sporadic manifestations, but unquestionably signs of the times. The opening of the new century is in reality a year of very serious awakening to those Englishmen who are not deaf to the voices in the air around them. It is rapidly dawning upon many that "the greatest empire which the world has ever seen" cannot be maintained unless we cast off insular prejudices and traditions, and make a careful study of those points in which other nations are our superiors, with a view to the intelligent adaptation and development, as distinguished from mere imitation, of their methods to our own particular needs.

The survey of the British chemical world at the dawn of the Twentieth Century affords, however, scope for satisfaction in many ways. Not only have the places in which higher chemical work can be and actually is carried on been greatly multiplied, but the number of workers has been largely increased; and although the enthusiasm of these workers cannot well be greater than that of those who laboured so successfully twenty years and more ago, it has not become diminished, and is certainly diffused more widely amongst the *personnel* of our colleges and universities. In this connection I need only remind you of the large number of active and independent investigators who are to be found amongst the members of the junior staff at almost every college in the country, and which is altogether without parallel in the past.

There are hardly any of the great problems now exercising the minds of chemists throughout the world which are not being worked at by some of our number; whilst that some chapters in the recent progress of chemical science are more or less specifically British, I would only remind you of the isolated labours of Dr. Perkin in the field of magnetic rotatory power; of Sir William Crookes's exploration of the phenomena occurring in high vacua; of the researches of Abney, Russell, and Hartley on the absorption spectra of organic compounds; of the investigations by Harold Dixon and Brereton Baker of the behaviour of substances in the complete absence of moisture; of the extension by Pope and Smiles of our knowledge of asymmetric atoms; of the near approach to the absolute zero of temperature by Dewar; and of those marvellous discoveries of Rayleigh and Ramsay which have not only introduced us to five new aërial elements, but have revealed the existence of a hitherto unknown type of matter, which is apparently incapable of entering into chemical combination at all.

But whilst we may thus congratulate ourselves on this increased activity in chemical investigation, and upon the maintenance of a high standard of quality by the exceptional brilliancy of the researches of some of our number, we must now carefully consider how we stand with regard to the absolute quantity of our output.

I have called your attention to the evidence of activity in the British chemical world which is furnished by the number of original investigations communicated to the Chemical Society of London. Let me now ask you to turn to the corresponding picture, which is furnished by the statistics of the much younger Chemical Society of Berlin.

Original Communications to the Chemical Society of Berlin.

1868 ..	97	1879 ..	604	1890 ..	630
1869 ..	252	1880 ..	563	1891 ..	677
1870 ..	277	1881 ..	495	1892 ..	553
1871 ..	288	1882 ..	541	1893 ..	587
1872 ..	303	1883 ..	535	1894 ..	653
1873 ..	420	1884 ..	646	1895 ..	636
1874 ..	516	1885 ..	686	1896 ..	566
1875 ..	488	1886 ..	696	1897 ..	560
1876 ..	517	1887 ..	708	1898 ..	555
1877 ..	568	1888 ..	658	1899 ..	549
1878 ..	602	1889 ..	601	1900 ..	636

A comparison between these figures and those of the London Chemical Society is best effected by means of a diagram, which speaks for itself, and shows that chemical science occupies an entirely different place in Germany from that which it even now does in this country. The curves in this diagram bear, indeed, somewhat the same relationship to each other as do the homely elevations of the Grampians to the snow-clad peaks of the Andes.

Is this state of affairs to continue throughout the Twentieth Century? Are intellectual ambitions to be for

ever subordinated to the extension of territory, to the acquisition of that metal which has had its atomic weight so accurately determined by Thorpe and Laurie, and to those other problems which fill the political horizon? Even the most recent awakening of interest in higher scientific education is not altogether of the breed to satisfy us as men of science; for the interest is assuredly not in the pursuit of knowledge for its own sake, but is aroused by the desire to secure those material advantages which it is beginning to be realised must inevitably result from the steadfast prosecution of scientific research. This is indeed a very different spirit from that which has led to the proud position occupied by science and learning of all kinds in Germany.

Schiller has truly said—

"Knowledge is to one a goddess, to another only an excellent cow."

I fear there can be no doubt that here it is the cow, and not the goddess, that is in request. Thus, whilst in Germany the love and reverence for knowledge preceded the esteem of knowledge for the material benefits which it confers, we must hope that in our country the eagerness to secure the material advantages will perhaps lead to a love and reverence for that which confers them, so that in the course of time, perhaps, the useful cow will be allotted a stall on Olympus, or be at least pastured on the grass of Parnassus.

From whatever motive, whether utilitarian or otherwise, we wish to see the position of science in this country raised, and the qualitative and quantitative output of scientific work increased, I imagine that the methods to be immediately pursued for attaining this end must be very similar.

If the higher teaching of science is to be really encouraged the first necessity is that this higher teaching shall offer a sufficiently attractive career to the man of ambition as well as to the enthusiast. We all know that the supply of enthusiasts of intellectual power combined with capacity to perform is extremely limited and wholly inadequate for carrying out the important work of the world, and that the greater part of such work is actually done by men of ambition.

In order that the academic world may attract the ablest men of ambition as well as that *rara avis*, the able enthusiast, it is necessary that the highest prizes for academic distinction should carry similar social prestige, similar remuneration, and similar opportunities of exerting public influence as are enjoyed by the leaders of other professional callings; they should be at least equal to those of the Archbishop of Canterbury or of the Lord Chancellor. It is not by any means necessary that such prizes should be numerous, as is abundantly demonstrated by the volume of able ambition which is drawn into the Church and to the Bar by the comparatively few opportunities for great success in those professions. The enthusiasts already find their way into the academic world; and, although they maintain the quality of British scientific work, they are unable, by virtue of their scarcity, to maintain the quantity which is essential for the luxuriant growth of science in our midst, whilst the absence of such tangible rewards as are bestowed in other spheres of intellectual activity prevent the importance of science being recognised by a public which has no appreciation of the inward and spiritual grace unless guided by the outward and visible sign.

Precisely the opposite policy, as far as remuneration is concerned, has, however, been pursued in the academic world during recent years, the few very moderate prizes which formerly existed having been deliberately commandeered to more nearly equalise the value of the chairs in all departments.

The principle of equalising the remuneration of different chairs is as inequitable as it is utterly unsound from a business point of view. The principle is unsound because equal salaries will not secure men of similar standing in different subjects, it is inequitable because the amoun o work attaching to the chairs of different subjects is necessarily very unequal, as is the order of intellect required for the successful discharge of their duties.

Again, the system which is gaining ground in this country of allocating a certain stipend to a chair is unbusinesslike and mischievous. It is as irrational to fix the remuneration of a particular chair as it would be to fix the price to be paid for one's portrait, irrespectively of whether it were taken by a photographer or painted by a Royal Academician. If we really want the best man for any particular professional service, whether it be to treat us for a disease, to plead our cause in a court of law, or to perform on some musical instrument for our delectation, we know we must make up our minds to pay the price which the best man commands in his particular profession, and it is absurd to suppose that the same principle does not hold good in the matter of securing the best man for an academic appointment. This, again, is intimately connected with the desirability of providing a sufficient number of steps in the academic ladder, so that it shall not be possible for the "young man of promise" to be rushed into a first-class appointment from which he has no ambition to move for the remainder of his days.

Another matter, again, requires consideration; if we are really in earnest in the attempt to bring our universities abreast of those in other countries, our chairs must be systematically thrown open to the whole world, and the best men obtainable secured, irrespectively of their nationality. Not only have small nations adopted this plan, but even the nation which is pre-eminent for its academic strength is by no means blind to the importance of drawing into its service from the outside men of commanding brilliance and power. I need not remind you that England has also exhibited a wise and liberal spirit in this matter in the past, and that, as far as our science is concerned, this policy has been most fully justified. For, consider only what the English Chemistry of the latter half of the Nineteenth Century owes to the genius and magnetic influence of the imported Hofmann. I can imagine the electors to British chairs suggesting that there might be linguistic difficulties in the way of carrying out such a policy, in answer to which I would appeal to the pupils of Hofmann to say whether his stimulating discourse lost anything of its vigour and inspiration through the strong Hessian accent with which every word of it was saturated. It is to be hoped that no narrow and short-sighted policy, disguised under that too often mis-used word "patriotism," will seek to close the doors of our universities to the genius and ability of other nationalities.

I believe, however, that one of the most urgent and pressing of University reforms is that greater facilities should be afforded for the migration of students from one university to another, without prejudice to their acquisition of a degree. It is the present system, which practically chains an undergraduate with links of steel to the university at which he matriculates, that is at the root of many of the evils under which our higher education is labouring.

The university at which a youth matriculates is often determined by the fatuous, although pathetic, wish of the father that his son should spend his time, I will not say work, amidst the surroundings which awaken such pleasant memories in himself; and the youth once within the magic portals has little or no opportunity of rectifying the possible mistake of his fond parent, who has probably for a quarter of a century been quite out of touch with university matters, or even divorced from the intellectual world altogether.

This foolish sentiment of loyalty to a university or even college is sometimes kept up for generations, and I have met persons who have told me that their family had always been Balliol or Trinity men, with the same sort of pride that they would doubtless have informed me, had they been able, that their ancestors came over with the Conqueror, or had charged with the Cavaliers at Naseby

The prevalence of such a sentiment shows that our

universities are principally valued for their social attractions, as well as for their past history and ancient traditions, in which connection it is always well to remember that a living dog is better than a dead lion.

The possibility of students dissociating themselves from the university of their matriculation and freely migrating from one school to another would, in my opinion, not only be of immense advantage to the students themselves, enabling them to obtain the best instruction in each particular subject, and greatly extending their horizon and knowledge of the world, but it would operate most favourably on the universities themselves, minimising the tendency to stagnation, and compelling those who hold the purse-strings to provide for the strengthening of weak departments. Nor should the possibilities of migration be limited to the Universities of the United Kingdom, or even of the British Empire, but the prospect should be kept in view of ultimately effecting an arrangement whereby students could enjoy the advantage of visiting the universities of other countries.

Such migration is, of course, closely connected with the duration of the period of university study, and in this matter reform is most urgently needed. The traditional three years devoted to the acquisition of a degree is hopelessly inadequate for the higher purposes of university training, especially when the very immature age at which English students generally begin their university career is taken into consideration. The period of academic study should be forthwith extended to five years, as it is only in this way that the university can be effectively made a centre of research. Without a course of study of such duration, and of which research forms a part, it is quite impossible that the highly trained men who are now so urgently needed for practical avocations should be produced.

In this connection, again, we all know that much mischief has been going on in recent years. Instead of the terms on which degrees are at present obtainable being regarded as too lenient and easy, proposals are actually being put forward in some quarters to enable persons attending evening classes to thereby qualify for university degrees. Now, whilst it is of the utmost importance to provide abundant opportunities for the talented poor to obtain a university education by reducing the fees, and by instituting a sufficient number of bursaries, it is imperative that those who are to be stamped with the distinctive mark of a university should have devoted their whole and undivided attention, over a certain period of time, to the courses of study prescribed. Let us beware of introducing the half-time system into the university, a system which we know to be a deplorable makeshift even in the elementary school.

In this matter of the aspirations, scope, and functions of a university we have not merely to contend with the ignorance and apathy of the average Philistine, but we are wrestling against principalities, against powers, and against darkness in high places. Thus, only four months ago one of our most prominent statesmen, whose oracular and sporadic utterances inspire amongst millions almost the awe and respect which is felt for the supernatural, is reported in the columns of the daily papers to have said at one of the most important educational gatherings of this first year of the new century:—"You, Mr. Vice-Chancellor, spoke of the stigma that would rest on the University if it did not annually produce some work of original research. I, from another point of view, am contented if you do nothing of the kind. I am satisfied to think that in a large and increasing degree you will train men and women fit for the manifold requirements of this Empire." This statesman, who it is not surprising to find was educated at Eton and Oxford, is thus of the opinion to-day, unless, indeed, his views have changed in the interim, that it is possible to train men and women fit for the manifold requirements of this Empire without bringing, at any rate, some of them into contact with the living spirit of research—that spirit which, operating through the ages, has enabled man to transform the wilderness in which he was placed by his Creator into the garden of material and intellectual enjoyments in which that statesman was himself born.

I would ask you to contrast with the views of the distinguished *alumnus* of Eton and Oxford the utterance of another statesman who, unhampered by such educational antecedents, has formulated the following ideal for the guidance of that university which he has himself created:—

"The third feature to which I should call attention, and which, I am inclined to say, is of all the most important, is that a university should be a place where knowledge is increased, and where the limits of learning are extended. Original research, the addition of something to the total sum of human knowledge, must always be an essential part of our proposals."

Lastly, we have to consider whether this university work, in which we hope for such great developments in the Twentieth Century, is still to be carried on by what is virtually private enterprise and private endowment, or whether it is to be provided for by taxation.

If the reforms and developments which are being preached from so many platforms are to be really carried out, if even our higher scientific training alone is to be brought into line with that which is provided in many other countries, it is indubitable that expenditure will have to be enormously increased. Now, profoundly as we all admire the enlightened public spirit of the men and women who have in the past endeavoured out of their private resources to help forward the great movement of higher education, it is, I believe, the firm conviction of all who have any real knowledge of what this higher education means, and a clear conception of what must be done in order to put it on a proper footing in this country, that on private benefaction alone this work cannot be accomplished. But even if private endowment could raise this great edifice in our midst, it is obvious that we should have to wait indefinitely for its realisation. Voluntary contributions cannot be made to come at the bidding of those who stand in need, nor directed into the channels where they will produce the most good; they have to be patiently waited for, with the result that valuable time is lost and opportunities pass by never to return. Private benefaction, moreover, is almost always retrospective; a hospital is not founded by the charitable until the sick are dying unattended; almshouses and orphanages are not thought of until the widow and the fatherless are either starving in the streets, or begging on the doorstep. What we so forcibly recognise in this matter, however, is that we have not only to make up for leeway in the past, but that we must now exercise prevision to prevent similar disastrous lapses in the future. The state of affairs to which we have been reduced must not be allowed to occur again; the warnings of those possessing special knowledge in these matters must not be disregarded in the future as they have been in the past, for it is no exaggeration that the whole of the learned societies and academic bodies of this country put together have at present a smaller corporate share of political influence than a Temperance League or a Trades Union. To what has this state of things reduced us? The humiliating spectacle of "the greatest Empire the world has ever seen" at the beginning of the Twentieth Century without a teaching university in its Metropolis, and engaged upon the task of tardily patching one together out of those heterogeneous elements of uncertain valency which are to hand. Is the completion of this structure, on a scale challenging comparison with the universities which are to be found in the other great capitals of Europe, to be delayed until a millionaire, or rather series of millionaires, can be induced to finance it? To this work, and to other works like it, is it not fitting that every inhabitant of this country should contribute? For these are works which assuredly benefit all classes, not only of this generation, but of those which are to come—at least as much as the acquisition of territory at a distance of 8000 miles from home, and for which

purpose the nation is apparently willing to pay at the rate of one and a quarter million sterling per week for an indefinite period of time.

It is sometimes urged that this higher education does not benefit the masses; but could any contention be more erroneous? The poor have really a far greater stake in the prosperity of our home industries and commerce than the rich; for whilst the decay of our producing power will remove the very means of subsistence from the poor, it matters very little to many of the rich whether their dividends are derived from home-enterprises or from those of a Billion Dollar Combine, or some similar transatlantic Trust or Corporation.

Higher education and true universities are also amongst the most potent factors in breaking down the hereditary stratification of society, and in minimising the advantages depending upon the accident of birth, so that, with the greatly enhanced facilities which must be provided for students without means, they should afford in the future, even more than they have done in the past, an avenue for the humblest boy of talent to that position which he is by natural endowment and by his own exertion best fitted to fill in the interests of the State.

Is this great work of raising up a worthy system of national higher education, and of creating a living interest and widely diffused enthusiasm for knowledge, and for the increase of knowledge in all its branches, going to be accomplished during the century of which we have but crossed the threshold? Even the most sanguine among us dare not unhesitating say yes; but assuredly upon the answer, which is hidden by the veil of the inscrutable future, depends in the very highest degree, not only the material and intellectual welfare of the rising generations, but also the good name and reputation of the Empire in our own time, and the gratitude which, above all things, we should strive to earn from that immortal part of us which we call Posterity.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING AUGUST 31ST, 1901.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, September 9th, 1901.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 208 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from August 1st to August 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 208 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during the month was 2·12 inches, the average fall being 2·38 inches; this leaves a deficit of 0·26 inch, and raises the total deficit for the year to 0·39 inch, or 2·5 per cent on the thirty-five years' average.

Our bacteriological examinations of 545 samples have given the results recorded in the following table; we have also examined 39 other samples, from special standpipes, &c., making a total of 584 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	284
New River, filtered (mean of 130 samples) ..	13
Thames, unfiltered (mean of 26 samples) ..	1646
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 299 samples)	22
Ditto ditto .. .. highest	280
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 26 samples) ..	223
River Lea, from the East London Company's clear-water wells (mean of 38 samples) ..	16

Of the 467 samples of impounded and filtered water supplied to London and examined bacteriologically during the past month, 22 samples, or 4·7 per cent, were sterile. Five samples contained more than 150 microbes, and six samples, or 1·2 per cent, contained more than 100 microbes per c.c. The mean number of microbes in the six excess samples was 212, against a corresponding mean of 173 in the 31 excess samples of July.

These figures show that the London Water Supply is quite on a level with its normal high standard of excellence.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

CONTRIBUTIONS TO THE SCIENCE OF THE NITROCELLULOSES.*

By G. LUNGE and J. BEBIE.

(Continued from p. 134).

G. *The Influence of the Nitrous Acid contained in the Nitric Acid on the Stability of Gun-cotton.*

IN the industry of the nitroglycerin and nitrocellulose explosives, the idea prevails that the presence of nitrous acid in the nitration mixtures tends to diminish the yield as well as the stability of the products generated.

There was to be found only a single research published on this point, and this, dating from year 1847, was by Payen. This experimenter states that nitrous acid diminishes the yield as well as the proportion of nitrogen in the nitrocellulose. Apparently no fresh research was undertaken in this connection for more than fifty years.

It is certainly not improbable that the action of nitrous acid diminishes the stability. In the nitration mixtures of nitric acid and concentrated sulphuric acid used in the manufacture of gun-cotton, the greater part of the nitrous acid must be present as nitrosyl-sulphuric acid. But as the reaction $N_2O_4 + H_2SO_4 = SO_3NH + HNO_3$ is reversible, there is always to some extent some free nitrous acid present.

This circumstance is of great practical importance, for if the nitrous acid should indeed exert the injurious influence, as is supposed, the manufacture of nitric acid must be conducted with greater care than heretofore. But there were always experimenters who were of opinion that the nitrous acid was by no means injurious, and it seemed advisable to resume the research carried out half a century ago, which was therefore started a few years ago in this laboratory.

Lunge and Weintraub state that with less than 6·5 per cent nitrous acid in the nitric acid (which in practice is the maximum amount present), the N_2O_4 exerts no appreciable influence. A small difference was only noticeable

* *Zeitschrift fur Angewandte Chemie*, 1901, Heft 20.

when the nitrous acid rose to 12 per cent, the nitrogen of the gun-cotton then sinking to 210·78 c.c. The stability of the products was not then tested. It therefore remained for us to proceed with stability relationships.

It is not yet clear as to which is the most reliable test of stability. In order to decide which was best suited to our purpose, we had next to make comparisons between the different methods.

In their underlying causes and actions, the stability relationships of gun-cotton are so far insufficiently known to us. Hence it happens that the methods adopted for its examination are more or less empirical, and afford no absolute values.

The measure of stability usually taken is the time during which a certain quantity of the explosive can be maintained at a certain temperature till the first trace of decomposition sets in. This shows itself in the production of nitric acid, which is detected by an indicator. The universal "heat test" of Abel is based upon this principle. Potassium iodide is used as indicator in this case.

As this reaction may be obscured by certain by-products of the explosive, Osk. Guttmann substituted a new reagent, viz., diphenylamine. At the beginning of the reaction, a yellow zone is first formed on the moistened part of the test-paper, and after one to two minutes a blue band should suddenly appear on the dividing line between damp and dry. But, according to Thomas, this blue colouration established itself quite gradually; and we ourselves, after numerous determinations, could not get the sudden appearance of the blue line. Shortly after the production of the greenish yellow zone, a bluish tinge was visible, which became intensified in the course of a few minutes. By taking as a standard a certain degree of intensity of the blue colour, sufficiently accurate results may be obtained by this method.

On the other hand, Spica rejects the diphenylamine test, neither could he confirm the sudden appearance of the blue zone. Hence, Spica proposes another reagent, viz., metaphenyldiamine, which is said to be considerably more sensitive than the other. We rather doubt that this is of any advantage. As this part of our work was already concluded before the appearance of Spica's results, we carried out no determinations with this method.

The material used in these experiments had necessarily to correspond in stability to practical requirements. Hence it had next to be determined how to attain this in the production of gun-cotton on the small scale. This question stands in intimate relation with that of the cause of instability. Formerly the latter was attributed entirely to residual traces of the nitration acids; and hence it would be only necessary to remove the latter by washing. The once frequent explosions in gun-cotton factories have thoroughly proved that stability is not to be obtained by lengthened washing in cold water, or even in running water; and Abel's method is now universally adopted, in which the nitration products are pulverised and washed with boiling water.

(To be continued).

THE ESTIMATION OF CARBONIC ACID IN WATER.*

By JOSEPH W. ELLMS and JAY C. BENEKER.

(Continued from p. 103).

Lunge-Trillich or Seyler Method.

THIS method depends on the action of phenolphthalein as an indicator in the presence of free carbonic acid, and of carbonates and bicarbonates of the alkaline earth bases; and on the assumption that in the bicarbonates of these bases there is one molecule of half-bound carbon dioxide for each molecule of fixed carbon dioxide.

Leeds (*Journ. Amer. Chem. Soc.*, 1891, xiii., 98), in this country, and Trillich in Europe, proposed, at about the same time, the determination of the free carbonic acid in water by titrating the sample with a solution of sodium carbonate, using phenolphthalein as the indicator. The sodium carbonate reacts with the free carbonic acid to form sodium bicarbonate. As soon as the free acid is neutralised, any further addition of sodium carbonate produces a pink colour. This affords a direct means for estimating the free carbonic acid without involving the half-bound. With waters which are acid to phenolphthalein, the determination of the fixed carbonic acid by Hehner's method gives at once the half-bound carbonic acid according to the assumption stated in the preceding paragraph. With waters which are alkaline to phenolphthalein, by the determination of this "phenolphthalein alkalinity," and the "total alkalinity" obtained with lacmoid as the indicator, the amount of half-bound carbonic acid can easily be estimated. In the latter case of course free carbonic acid is absent.

Seyler, who has made a study of this method, considers it one which gives accurate results, and one which is free from many of the difficulties involved in Pettenkofer's and Trillich's methods. The chief criticism of the method seems to have been as to the correctness of the assumption for quantitative purposes, that, when a water was acid or neutral to phenolphthalein, there was present for each molecule of fixed carbonic acid, one molecule of half-bound carbonic acid; and to the claim that when the water was alkaline to phenolphthalein, only one-half the carbonic acid in the form of the normal carbonates was determined by titrating with acid to the discharge of the colour produced by this indicator.

If to 10 c.c. of a cold 0·02 normal solution of sodium carbonate, phenolphthalein be added, and then a 0·02 normal solution of sulphuric acid, it will be found that only 5 c.c. of the latter are required to discharge the colour. The reaction is as follows:—

$$2Na_2CO_3 + H_2SO_4 = 2NaHCO_3 + Na_2SO_4.$$

The pink colour produced by the phenolphthalein in the sodium carbonate solution is destroyed when one-half the latter becomes saturated with the carbonic acid liberated by the mineral acid; and this occurs when one-half the base has been neutralised. It is therefore evident that bicarbonates of the fixed alkalis are neutral to phenolphthalein.

The assumption that carbonates of the alkaline earth bases react in an analogous manner, is, so far as we can ascertain, correct, as the following experiments will show.

A calcium bicarbonate solution was boiled down to about one-third or one-fourth of its original volume, and allowed to cool out of contact with the air. The precipitated calcium carbonate settled out, only such remaining in solution as was soluble without the presence of any free or half-bound carbonic acid. Several portions of the supernatant liquid were withdrawn, and titrated with acid, using phenolphthalein as the indicator. The total alkalinity of the solution was also determined with the indicator lacmoid.

Action of Phenolphthalein as an Indicator in a Solution of Calcium Carbonate.

No	Calcium carbonate solution.	Sulphuric acid. N/50 (approx.). A.*	Sulphuric acid. N/50 (approx.). B.†
	C c.	C.c.	C.c.
1	100	1·65	3·15
2	100	1·65	3·25
3	100	1·50	3·10
Average		1·60	3·17

* To discharge pink colour with phenolphthalein.
† To obtain end-point with lacmoid.

A solution of magnesium carbonate acted similarly, 1·65 c.c. of acid being required to discharge the pink colour formed with phenolphthalein, and 3·4 c.c. to obtain the end-point with lacmoid. The reaction involved in these

* *Journal of the American Chemical Society*, xxiii., No. 6.

two cases is doubtless analogous to the one which takes place in sodium carbonate solutions, viz.,

$$2CaCO_3 + H_2SO_4 = Ca(HCO_3)_2 + CaSO_4.$$

It was found that these solutions of calcium and magnesium carbonate were very sensitive to the absorption of carbon dioxide from the air, even on a very short exposure; and also that it was extremely difficult to free them from the last traces of the half-bound carbonic acid. Only by violent and prolonged boiling and cooling out of contact with the air could this be accomplished. A calcium carbonate solution, which after boiling was cooled in air free from carbon dioxide, required for 100 c.c., 1·5 c.c. of acid with phenolphthalein as the indicator, and 3·1 c.c. with lacmoid. A portion of the same liquid cooled in a beaker required 0·95 c.c. of acid with phenolphthalein, and 3·2 c.c. with lacmoid. Magnesium carbonate solutions absorbed carbon dioxide more slowly, as has been previously pointed out.

Hot solutions of calcium carbonate and of magnesium carbonate do not react to phenolphthalein in the same manner as do these cold solutions, since in the former the bicarbonates formed by the liberation of the carbonic acid from the normal carbonates are immediately decomposed by the heat with evolution of carbon dioxide. It is therefore possible to determine the whole of the carbonates of the alkaline earth bases even with phenolphthalein as the indicator, provided the solution is kept boiling. The same is true of the carbonates of sodium and potassium. But phenolphthalein is by no means a good indicator for this purpose, and the results are much more accurately obtained with lacmoid or one of a similar character.

It has been considered probable that sodium carbonate in solution undergoes hydrolysis in the following manner:—

$$Na_2CO_3 + H_2O = NaHCO_3 + NaOH.$$

As the sodium bicarbonate thus formed supplies no hydrogen ions, and the sodium hydroxide is dissociated, producing a large number of hydroxyl ions, the solution is therefore quite strongly alkaline. To phenolphthalein it exhibits the alkalinity characteristic of caustic alkaline solutions. It may be that a similar hydrolysis takes place in the case of calcium carbonate and magnesium carbonate solutions.

$$2CaCO_3 + 2H_2O = Ca(HCO_3)_2 + Ca(OH)_2.$$

If this does occur it readily explains why calcium and magnesium carbonate solutions are alkaline to phenolphthalein, and why they show the same evidence of the presence of hydroxyl ions as in the case of sodium carbonate solutions.

(To be continued).

THE DISSOCIATING POWER OF DIFFERENT SOLVENTS.*

(A Summary).

By HARRY C. JONES.

(Continued from p. 136).

Organic Solvents (continued).

Pyridine.—Our knowledge of the dissociating power of pyridine we owe almost entirely to St. v. Laszczynski and St. v. Gorski (*Zeit. Elek. Chem.*, iv., 290). They measured the conductivities of lithium chloride, potassium, sodium, and ammonium iodides, and potassium, sodium, and ammonium sulphocyanates in pyridine, over a wide range of dilutions. A few of their results are given:—

Potassium iodide.		Sodium sulphocyanate.	
v.	μv.	*v.*	μv.
178·49	22·04	32·24	7·98
713·9	30·68	128·96	12·79
2855·6	38·05	515·84	20·56

The conductivities are very considerable in this solvent.

* *American Chemical Journal*, xxv., No. 3.

Werner (*Zeit. Anorg. Chem.*, xv., I., 39), found that certain inorganic salts in pyridine conduct very well, and yet show little or no dissociation by the boiling-point method.

Other Organic Solvents.—A few measurements of the conductivity of one or more substances in a number of solvents have been made, but the work with any one of the remaining solvents is so slight that it does not call for special treatment. Thus, Werner (*Zeit. Anorg. Chem.*, xv., I., 39), found that cuprous chloride in ethyl sulphide conducts very poorly. Cattaneo (*Biebl. Wied. Ann.*, xvii., 365), studied a few solutions in glycerin, and found that they had larger conductivity than the corresponding solutions in ether. They also had larger temperature coefficients of conductivity. Kablukoff (*Zeit. Phys. Chem.*, iv., 429), measured the conductivity of hydrochloric acid in benzene, xylene, and hexane, and showed that solutions in the hydrocarbons conduct very poorly.

Dutoit and Aston (*Comptes Rendus*, cxxv., 240), measured the conductivity of electrolytes in benzene chloride, ethyl iodide, ethyl bromide, and amyl acetate, and found that solutions in these solvents conducted very poorly. They found, on the other hand, that solutions in nitroethane conduct very well. Dutoit and Friderich (*Bull. Soc. Chim.*, [3], xix., 325), worked with acetophenone as solvent, and with cadmium iodide, mercuric chloride, and ammonium sulphocyanate as electrolytes. The conductivity in this solvent was small.

Four other solvents have thus far been studied—ethyl acetate, ethyl acetoacetate, benzaldehyde, and nitrobenzene. This work has been done by Kahlenberg and Lincoln (*Journ. Phys. Chem.*, iii., 12). As electrolytes they used ferric and stannous chlorides, bismuth trichloride, and antimony trichloride. The conductivities in these solvents are, in general, small, but vary considerably with the nature of the electrolytes used.

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadatres des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 7, August 12, 1901.

The Colour of Ions.—G. Vaillant.—The author performs a series of experiments on the absorption spectra of solutions of permanganates of potassium, barium, and zinc, and he verifies the following statements. (1). In completely dissociated solutions, only containing one coloured ion, the colouration is independent of the nature of the other ion. (2). If, on the contrary, ionisation is incomplete, the colouration varies with the nature and the concentration of the colourless ion. (3). The colouration of a solution of any concentration whatsoever is usually connected with its degree of dissociation, and this connection is expressed by a formula of two variables and two only, one characterising the complete molecule and the other the dissociated molecule.

The Value of Molecular Weights at the Temperature of Ebullition.—M. de Forcrand.—Some months ago the author stated the following general law. "In all chemical or physical phenomena the heat of solidification of a molecule of any gas whatsoever is proportional to the absolute temperature of ebullition under atmospheric pressure." He now notices one of the consequences of this general relation, by examining bromine, iodine, mercury, nitric acid, and nitric anhydride, and finds, particularly from a study of the last example, a remarkable agreement existing between the results now obtained and those already published. His researches on the properties of the above examples allow of the calculation of the rela-

tion between the molecular weight (M) and the temperature (T).

Action of Benzoyl Chloride on Trioxymethylene in presence of Zinc Chloride.—Marcel Descudé.—In a preceding research the author showed that zinc chloride considerably facilitates the union of acetyl chloride with the methylic and ethylic aldehydes. By the action of benzoyl chloride on trioxymethylene, he prepared a compound corresponding to the formula $C_{14}H_{12}O_4$. He discovered since that this formula is inexact and ought to be replaced by the following, $C_{15}H_{12}O_4$, which represents the composition of methylene dibenzoate—

$$\begin{matrix} C_6H_5-COO \\ C_6H_5-COO \end{matrix}\!\!>\!CH_2.$$

He now attempts to combine directly benzoic anhydride and methanal, and prepares methylene dibenzoate by this method in a pure crystalline state. These crystals are doubly refracting and melt at 99° to a colourless limpid liquid, which boils at 255°.

No. 8, August 19, 1901.

Researches on the Mechanism of Etherification in Plants.—E. Charabot and A. Hébert.—The authors believe that in plants etherification is produced by the direct action of acids on alcohols; this is favoured by a particular agent which plays the part of dehydrator. Various experiments were made on the terpenic compounds and the following conclusions drawn. (1). Under the pure and simple action of acetic acid, linalol is etherified with extreme slowness, only in plants. (2). Terpenic alcohols, which under the influence of an acid are etherified more easily, are also those which vegetables contain in the largest proportion combined with the same acid. (3). For the same terpenic alcohol, the acid combining the most easily with this alcohol is that whose ether is the most abundant in the plant. (4). When two alcohols co-exist in a vegetable, if these two alcohols are etherified, the acid divides itself between them in the same proportion as they are present in the plant.

MISCELLANEOUS.

British Association for the Advancement of Science.—The following are the names of the Officers and Committee of Section B (Chemistry) at the Glasgow Meeting of the British Association :—

President—Prof. Percy F. Frankland, F.R.S.

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Secretaries—Dr. W. C. Anderson, M.A.; Dr. G. G. Henderson, M.A.; Prof. F. S. Kipping, F.R.S.; Prof. W. J. Pope; Dr. T. K. Rose (Recorder).

Committee—Sir W. Roberts-Austen, LL.D., F.R.S.; G. T. Beilby; C. H. Bothamley; Adrian Brown; Prof. Campbell-Brown; Prof. Dobbie; Prof. H. B. Dixon, F.R.S.; Prof. W. R. Dunstan, F.R.S.; Prof. J. Gibson; Dr. J. H. Gladstone, F.R.S.; Dr. A. G. Green; Dr. W. T. Lawrence; Prof. Hartley, F.R.S.; Dr. E. A. Letts; Prof. Willy Marckwald; Dr. Forster Morley; Prof. H. M'Leod, F.R.S.; Dr. W. H. Perkin, sen., F.R.S.; Prof. T. Purdie, F.R.S.; Prof. W. Ramsay, F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; Prof. J. Sakurai, LL.D.; Dr. M. W. Travers; Prof. J. M. Thomson, F.R.S.; Prof. Paul Walden.

The Papers brought before the Section were as follows :—

President's Address—The Position of British Chemistry at the Dawn of the Twentieth Century.

Dr. W. T. Lawrence—Duty Free Alcohol. (Followed by a Discussion).

Dr. A. G. Green—The Coal Tar Industry.

Report of the Committee on preparing a New Series of Wave-length Tables of the Spectra of the Elements.

Prof. Adrian Brown—Enzyme Action.

Prof. W. Marckwald—Radium.

Report of the Committee on the Relation between the Absorption Spectra and Chemical Constitution of Organic Substances.

Prof. E. A. Letts—Chemical Changes during Contact of Sewage with Bacteria.

Dr. S. Rideal—Humus and the Irreducible Residue in the Bacterial Treatment of Sewage.

Dr. S. Rideal—Sulphuric Acid as a Typhoid Disinfectant.

W. Thomson—Arsenic in Beer.

W. Ackroyd—Inverse Relation of Chlorine to Rainfall.

W. Ackroyd—The Distribution of Chlorine in Yorkshire.

Dr. J. H. Gladstone and *G. Gladstone*—Hydration of Tin, including the Action of Light.

Dr. J. H. Gladstone and *J. Hibbert*—Transitional Forms between Colloids and Crystalloids.

Report of the Committee on the Nature of Alloys.

G. T. Beilby—Minute Structure of Metals.

Prof. A. Michael—On the Three Stereomeric Cinnamic Acids.

Prof. A. Michael—On the Genesis of Matter.

Prof. A. Michael—On the Process of Substitution.

Prof. W. H. Perkin, F.R.S.—On the Synthetical Formation of Bridged Rings.

Prof. G. G. Henderson and *R. H. Corstorphine* — The Condensation of Benzil with Dibenzyl Ketone.

Dr. W. R. Hodgkinson and *L. Limpach*—Some Relations between Physical Constants and Constitution in Benzenoid Amines. Part III.

Dr. George Young—The Existence of certain Semicarbazides in more than one Modification.

Report of the Committee on Isomeric Naphthalene Derivatives.

Report of the Committee on Isomorphous Derivatives of Benzene.

Prof. J. Sakurai—Some Points in Chemical Education.

W. Thomson, F.R.S.E.—On the Detection and Estimation of Arsenic in Beer and Articles of Food.

Prof. James Walker, F.R.S.—On the Nomenclature of the Ions.

Dr. E. F. Armstrong—The Equilibrium Law as applied to Salt Separation and to the Formation of Oceanic Salt Deposits.

Report of the Committee on the Bibliography of Spectroscopy.

Dr. J. Gibson—The Electrolytic Conductivity of Halogen Acid Solutions.

P. J. Hartog—The Flame Colouration and Spectrum of the Nickel Compounds.

Dr. Farmer—The Methods of Determining the Hydrolytic Dissociation of Salts.

Dr. T. S. Patterson—The Influence of Solvents on the Rotation of Optically Active Compounds.

The Congress of the International Association for Testing Materials was held at Budapest on September 9th to 14th, under the presidency of Professor L. von Tetmajer, and was largely attended by engineers from all parts of the world. The delegates present included four from England, forty-one from Austria, three from Belgium, nine from Denmark, two from the United States, thirty-six from France, one hundred and fifty-two from Hungary, seventy from Germany, three from Norway, twelve from Italy, twenty-six from Russia, one from Roumania, three from Spain, one from Servia, ten from Switzerland, and five from Sweden. After an Inaugural Presidential Address and address of welcome from the Hungarian authorities, a representative of each country was elected an honorary president of the Congress; Mr. Bennett H. Brough being chosen for England, and Prof. H. M. Howe for the United States. The other English and American members present were:—Sir William H. Bailey (Manchester), Mr. Bertram Blount (London), Dr. C. J. Renshaw (Ashton-on-Mersey), and Dr. R. Moldenke (New York). In

addition to the various reports of committees dealing with technical problems, the following papers dealing with Metals were read and discussed:—"On the Measurement of Internal Tension," by M. Mesnager (Paris); "On the Forms of Carbon in Iron," by Baron Jüptner (Leoben); "On Brinell's Researches," by M. A. Wahlberg (Stockholm); "On the Testing of Metals by means of Notched Bars," by M. H. Le Chatelier (Paris), by M. G. Charpy (Paris), and by Professor Belelubsky (St. Petersburg); "On Micrographical Researches on the Deformation of Metals," by M. F. Osmond (Paris); "On Metallography," by M. E. Heyn (Charlottenburg); "On the Testing of Railway Material," by M. E. Vanderheym (Lyons); and "On the International Iron and Steel Laboratory," by Professor H. Wedding (Berlin). Several papers dealing with stone and mortars were also read, and an interesting lecture on the Iron Industry of Hungary was delivered by Professor Edvi-Illes (Budapest).

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DAVID LEWIS, Treasurer.

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J. S. REDMAYNE, B.A., Secretary.

THE CHEMICAL NEWS.

Vol. LXXXIV., No. 2183.

HUMUS AND THE SO-CALLED IRREDUCIBLE RESIDUE IN BACTERIAL TREATMENT OF SEWAGE.*

By SAMUEL RIDEAL, D.Sc.(Lond.), F.I.C.

Organic decompositions, except those of final oxidation, are usually attended by the production of a brown colour; the colouring matter sometimes remaining in solution, and sometimes in the more energetic reactions separating in brown flakes. Types of reactions producing the colour are:—

1. Heating alone, as in the formation of caramel from sugar and its allies.

2. Heating with acids, alkalis, various salts, or even to a high temperature with water alone.

3. The change that occurs when vegetable tissues are injured or exposed to air, as seen when fruits are cut or bruised, connected with the action of the ferments called by Bertrand "oxydases."

4. Natural decay in the formation of soils, vegetable mould, and peat, and finally under certain conditions of lignite and coal.

Simultaneously with hydrolysis a smaller number of molecules seem almost invariably to undergo the opposite change of withdrawal of water, accompanied by increase in the percentage of carbon, and condensation of the molecule, producing coloured colloid compounds, which are comparatively inert, but have the power of combining with, or mordanting, large quantities of the matters in solution, both inorganic and organic. It is probable that the molecular weight of these bodies is exceedingly high. Their separation and purification is so difficult that in spite of a large amount of work it has not yet been satisfactorily accomplished, but many common properties besides colour render it convenient to group together under the aggregate term *humus* all bodies possessing such properties and produced by dehydration with limited oxidation.

Crude humus can in nearly all cases be divided into three parts:—

I. Insoluble in alkalis, but combining with them = humin or ulmin.

II. Soluble in alkalis, and re-precipitated by acids = humic or ulmic acids.

III. Soluble in alcohol = resinoid bodies and so-called phlobaphenes.

Crenic and apocrenic acids are other names due to Berzelius, and more especially applied to the humous matters combined with iron in ferruginous waters and in bog deposits.

There is little doubt that the primary nucleus of all these bodies is non-nitrogenous, as it can be obtained from sugar and other substances free from nitrogen. H. Snyder (*Journ. Amer. Chem. Soc.*, 1897, xix., 738), compared the varieties of humus obtained from different organic matters kept out of contact with air for a year. He gives the accompanying figures for humus (see next col.).

C. V. John (*Zeit. Kryst. Min.*, xxiii., 289) found at the outcrop of a coal seam in Bohemia a native non-nitrogenous humic acid completely soluble in alkalis, and re-precipitated by acids of the composition C 54·98, H 4·64, O 39·98, ash 0·40.

Samples of peat examined by Tacke and Tollens (*Bied. Centr.*, 1900, xxix., 508) contained in the organic matter

Humus from—	C.	H.	N.	O.	Ratio of C. to N.
Cow manure	41·95	6·26	6·16	45·65	6·7
Green clover	54·22	3·40	8·24	34·14	6·6
Meat scraps	48·77	4·30	10·96	35·97	4·4
Wheat flour	51·02	3·82	5·02	40·14	10·1
Oat straw..	54·30	2·48	3·50	40·72	21·7
Sawdust	49·28	3·33	0·32	47·07	54·0
Sugar..	57·84	3·04	0·08	39·04	—

Native varieties gave the following percentages:—

					Ash.
Rich prairie soil ..	45·12	3·67	10·37	28·60	12·24
Cultivated soil.. ..	48·16	5·40	9·12	33·16	4·16
Never cultivated ..	44·12	6·00	8·12	35·16	6·60
Cultivated forty years	50·10	4·80	6·54	33·66	4·90

54·5 to 57 per cent of C, and 3·96 to 6·86 per cent N; an average ratio of N to C of 1 to 10. André (*Comptes Rendus*, 1899, cxxviii., 513), found the ratios of C to N in the organic matter insoluble in dilute acid to be:—Peat, 9·4; cultivated soil, 6·6; moorland soil, 11·9; vegetable mould, 8·5. The form in which the nitrogen exists has been a subject of controversy. Mulder and Thénard believed it to be present in the form of ammonia, and Detmer (*Landw. Vers. Stat.*, xiv., 248), gives to humate of ammonium the formulua $(NH_4)_6C_{60}H_{48}O_{27} = 6{\cdot}42$ per cent N; C, 55·05; H, 5·50; O, 33·03; $C/N = 8{\cdot}57$

But, on the other hand, even long boiling of a nitrogenous humus with alkalis only liberates a portion of the nitrogen as ammonia. Berthelot and André (*Comptes Rendus*, cxii., 916), in their examination of the humus produced by the action of hydrochloric acid on sugar, found it to contain C, 66·41—63·91; H, 4·57—4·58; O, 29·02—31·61 ($C_{36}H_{14}O_{12}$ to $C_{36}H_{16}O_{14}$). It was insoluble in water and dilute acids. In alkalis it was partly soluble and partly insoluble; the insoluble was called *humin*, and the soluble *humic acid*. The insoluble part took up alkali (K, Na, Ba, Ca), from water, forming insoluble salts. The whole substance combined with about four molecules NH_3, producing a gelatinous insoluble matter which, after boiling with water and magnesia, retained a proportion corresponding to the formula $C_{72}H_{33}NO_{26}$, which is that of an amido-acid formed from two molecules of the original. Adding $4NH_3$ to the first formulæ would give percentages of N = 7·93 and 7·57; $C_{72}H_{33}NO_{26}$ = only 1·05 per cent N. Berthelot and André considered the brown matter to be an anhydride or mixture of anhydrides, and that the nitrogenous constituents of soils (*Bull. Soc. Chim.*, 1891, v., 643), are not ammonium salts, but amides, some insoluble, which are decomposed by boiling with acids or alkalis, giving ammonia, and more slowly in the cold. The same authors (*Comptes Rendus*, 1887, 833, 911), found that a field soil contained when dry 2·35 per cent C, 0·166 N, and 0·892 K_2O, *i.e.*, $C/N = 14{\cdot}1$, and N in the organic matter = 3·54 per cent. The NH_3 has here been largely replaced by K_2O, which bears a ratio to the organic molecule of 19 to 100, or 16 per cent in the whole salt. To show the stability of the potash compound, only 1·6 per cent of the potash was dissolved by treatment with three successive portions of water or of 2 per cent ammonia; a somewhat larger quantity was extracted by sugar solution, by water saturated with carbonic acid, or by dilute acids. Dilute HCl removed in the cold 4·48 per cent, and even by boiling for sixteen hours only 11·4 per cent was extracted.

A sample of humus mould contained when dry 9·58 organic carbon, 0·86 N, and 1·165 K_2O, $C/N = 11{\cdot}1$, N in organic matter = 4·5 per cent. It yielded about half its potash to dilute HCl.

Eggertz (*Bied. Centr.*, xviii., 75), investigated a large number of these brown amorphous residues, which he divides into "Mullkörper" from peat and soil, and "Humuskörper" from carbohydrates by acids. He finds that in nearly all chemical reactions they behave alike. According to him the mull substances besides C, H, N,

* Read before the British Association (Section B), Glasgow Meeting, 1901.

and O contain S, Fe, P in the organic molecule. Thirteen samples gave :—C, 40·86—56·18; H, 4·33—6·63; O, 25·09—37·98; N, 2·59—6·43; SiO_2, 0·37—10·47; P, 0·15—7·58; S, 0·55—2·09; Al_2O_3, Fe_2O_3, 0·38—3·90. "The silica is probably present as NH_4 silicate. Both mull and humus substances contain ash constituents which can scarcely be considered as mere inorganic impurities" as they cannot be washed out (?) "Besides the N present as ammonium-mull salts, they contain N which is not removed by repeated solution and re-precipitation. Eight samples containing 5·8 to 10·7 N, at the end retained 2·12 to 5·30 per cent. A great part is diffusible, hence would be taken up by plants. "The constituents derived from the oxidation of mull substances are more important as a natural source of plant nutrition than the mineral phosphates and silicates."

L'Hôte (*Journ. d'Agricult. Pratique*, 1890, 365) found in humic acid from garden soil 4·78 per cent N; from arable soils 6·07 and 5·41 per cent. Thénard obtained slightly higher figures with humic acid from rotted farm-yard manure. Sestini boiled crude humic acid with 2 per cent soda for thirteen and a half hours, and little more than half the nitrogen was expelled as ammonia, while only a relatively small amount of ammonia was formed by boiling with 10 per cent hydrochloric acid for twenty-four hours. By the action of nitrous acid he obtained evidence of the presence of amides, but a considerable portion must have been present in an organic state (*L'Orosi*, 1898, xxi., 1—6). He obtained furfuraldehyde by the action of hydrochloric acid on crude humus from soil, purified humic acid, and the humous substances obtained from sugar, showing another common property of the humous group.

In view of the extraordinary tenacity with which humous bodies retain inorganic constituents, there is no improbability in nearly the whole of the nitrogen being present in the ammonio- or at least amido-form. As showing this avidity of combination, Rodzanko (*Journ. Russ. Chem. Soc.*, xxii., 208), found that humin absorbs various inorganic substances from aqueous solution, as sulphates, chlorides, phosphates, and carbonates, salts of aluminium, and alkaline silicates, and that humic acid dissolves and decomposes several otherwise insoluble inorganic compounds, and decomposes silicates. "Humin compounds already containing a given element absorb substances containing this element more readily than other substances; it seems that metallic derivatives of humic acid are stronger acids than the original acid," depending on the poly-basicity and the formation of unsaturated acid salts. Bréal proved that an alkaline humate solution was directly absorbed by the roots of plants (*Ann. Agron.*, 1894, xx., 353).

A further light was thrown on the functions of humus, especially in connection with its occurrence in water and in sewages, by the researches of Adeney ("Dissolved Gases and Fermentative Changes," *Trans. Roy. Dub. Soc.*, September, 1895). A deep brown extract from peat by water and a little soda was allowed to ferment in air six months, then mixed with five volumes tap-water, and allowed to settle. It was known that peaty matters in river waters, having arrived at a stable condition in flow, suffered little oxidation or change. But, on the other hand, these substances, when fresh, undergo in water a considerable alteration, since the unoxidised peaty matter in upland surface water showed a ratio of carbon to nitrogen of 11·9 to 1, whereas after exposure to oxidation in lakes or large reservoirs the proportion was 5·9 to 1. These proportions of C to N are very similar to those found in the fermented matters resulting from the complete fermentation of sewage during slow sand filtration, *i.e.*, 9·6 : 1 to 6·3 : 1.

The fermented organic matter formed during slow filtration of sewage, besides showing similarly high proportions of C to N as peaty matter and similar resistance to fermentation, also resembles peat in colour and optical properties. Thus, when derived from a sewage filtrate of brown tint, the ratio of C : N was 7·1 : 1; it was not distinguishable from peat by the spectroscope (Hartley), giving identical ultra-violet absorption. Adeney early noticed that in every experiment in which oxidation of ammonia to nitric acid had been complete, small quantities of peaty or fermented organic matters were always present, that they were necessary for the *nitric* fermentation of ammonia, and that if absent, abundant nitrite, but no nitrate, was formed.

Experiments showed that in presence of large quantities of water and organisms, the peaty matter fermented to carbonic acid and nitric acid. If not diluted NH_3 *is absorbed*. In some experiments the oxygen of the peat itself must have taken part. *The peaty matter absorbs considerable quantities of ammonia.* An important conclusion of the research was that in the absence of peaty matters we get nitrous fermentation of ammonia, in their presence we get nitric fermentation of either ammonia or nitrous acid. "The presence of peaty or humous matters appears to preserve the vitality of nitric organisms during the fermentation of ammonia, and establishes conditions whereby it is possible for the nitric organisms to thrive simultaneously in the same solution with the nitrous organisms."

In a further research (*Trans. Roy. Dub. Soc.*, August, 1897), he established the similarity to peat and soil humus of the humus from fermented sewage. The latter was slowly but completely soluble in sodium carbonate, to a deep brown solution indistinguishable from that from peat or garden soil, the ratio of C to N being 6·84 : 1. Culture solutions of this were allowed to ferment in closed vessels; the action was slow, but the phenomena were :—CO_2 was produced, dissolved oxygen disappeared, there was no change in the free nitrogen, ammonia was converted into *nitrate*, and no nitrite was formed. Humus from peat behaved in exactly the same way. He concludes that "organic matters which are themselves the result of bacterial fermentative changes, or a carbon oxidation of fresh organic substances, take an active part in any subsequent fermentation of ammonium compounds with which they may be mixed, and determine the nitric fermentation of these compounds. . . The organic products of the first stage, or fermented organic matters, never give rise to the formation of ammonia," and therefore are generally non-offensive.

I have examined a number of these humous residues from the bacterial treatment of sewage. At the end of 1898 I found the peaty deposit in the Exeter septic tank to contain :—

Distance from bottom, inches	No. 1. 3.	No. 2. 9.	No. 3. 15.
Organic matter, per cent	32·35	32·40	31·31
Ash, per cent	67·65	67·60	68·69
Nitrogen, per cent	2·38	2·34	2·45
Percentage of N in organic matter	7·36	7·22	7·82
Ratio of carbon to one of nitrogen	6·8	6·9	6·4

Microscopical Characters.

1. Black amorphous matter; small sand particles; fragments of muscular fibre, dark coloured and corroded, and of other animal tissues; large amœba, cladothrix, micrococci, and bacilli; fragments of fæcal matter, vegetable tissue, and hairs.

2. Spiral vessels of a plant, anguillulæ, egg of an entozoom; fewer amœba, otherwise like the last.

3. Anguillulæ, vegetable hairs, and spiral vessels; fæcal fragments rather abundant; sponge spicules; animal hairs; no amœba and very few muscle fibres; otherwise like the preceding. It will be seen that the older matter is mixed with recent substances lately arrived in the tank.

I have also analysed the black deposit from the first-contact bed at Hampton (June, 1900); it contained :—

Water	7·18
Ash	48·37
Organic matter	44·45
	100·00

Total nitrogen	4·788
Percentage of N in organic matter	10·79
Organic nitrogen	3·058
Percentage of organic N in organic matter.	7·12
Combined ammonia	1·73
Ratio of carbon to one of nitrogen	7·0
The ash contained :—	
Oxide of iron and mineral salts	17·00
Coke	4·18
Siliceous matter	27·19
	48·37

The organic matter was therefore closely related to humus, and was similar to that found in the septic tank. A microscopical examination showed large numbers of anguillulæ, with amœbæ, a few rotifers and flagellate infusoria; aquatic larva cases and portions of insects; a few animal hairs (possibly human), and some isolated fragments of muscular fibre; diatoms and desmids (Synedra, &c.); vegetable débris; fragments of wood, epidermis, and leaf hairs; ducts of ferns, spiral vessels, straw and grass stems; a large quantity of dark brown amorphous matter of humous character; crimson particles and dyed fibres, blue and orange; fragments of coal and coke; sand; and carbonate of lime crystals.

Still more recently I collected some of the black floating particles from Stoddart's continuous filter at Knowle, Bristol (on September 28th, 1900). The total weight of deposit was 4·37 parts per 100,000 of effluent; it contained :—

Mineral matter	31·91
Organic matter	68·09
	100·00
Organic N	4·69
Combined ammonia	0·57
Percentage of organic N in organic matter	6·88
Ratio of C to one of N	7·3

The microscopic examination showed :—Aquatic larva cases, fragments of winged insects, numerous anguillulæ, crustacea (Daphnia), rotifers, infusoria (monas, paramœcium, vorticella), algæ (cladophora and species of conferva), cladothrix, beggiatoa, fungus mycelium, black particles (probably coke), brown amorphous matter, siliceous particles, vegetable hairs and fibre (*Trans. Soc. Engineers*, 1900, p. 247).

The finer portion of the organic matter collected from crude sewage by screening contains only 2 per cent of nitrogen. This low figure is of course due to the considerable quantity of undecomposed cellulosic matter present.

In 1901 I found in a number of dark muds from an estuary :—

Organic matter.	N % in organic.	Ratio C/N.
19·46	4·00	12·5
11·54	3·15	16·0
13·91	3·69	13·5
18·14	5·68	8·8
17·65	4·39	11·4
19·14	4·38	11·4
22·24	4·15	12·0
10·23	4·52	11·0
14·31	3·36	15·0
17·35	3·23	15·5
16·55	2·44	22·3
17·18	2·80	17·8

In conclusion, if sewage has undergone proper bacterial fermentation, the small quantity of peaty deposit, called by Cameron "burnt-out ash," and by others "irreducible residue," is of the nature of humus, and practically inoffensive. Kenwood and Butler state that at Finchley in 1900 the deposit from open septic tanks could be removed with little offence, and has been spread, without nuisance, over small areas of land in the neighbourhood. It has also the agricultural value of humus. Like peaty matters generally, it has a function in encouraging, when in small quantity, the nitrifying actions in the final oxidation, and itself undergoes slow oxidation to carbonic acid and nitrate.

SOME POINTS IN CHEMICAL EDUCATION.*

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Considered from a certain important point of view which, so far as I know, has not hitherto been explicitly stated, chemical education, as at present generally carried on, appears to me to be inefficient and unsatisfactory, and no better opportunity has presented itself, than on the present occasion, of submitting the matter to your consideration. It is for this reason that I wish to address you.

You are all aware that chemistry has made a marvellous and wonderfully rapid progress within the last fifteen years. Now, it is not my intention to dwell upon the ground on which the structure of modern chemistry, if I may so call it, stands, nor is it, indeed, necessary for me to do so, since its soundness is no longer disputed; it is rather to the fact that, in spite of the high educational value which it possesses, its teaching is unduly neglected, that I wish to draw your attention.

The recent progress in chemistry is characterised by the fact that not only experimental means of investigation have been extended, enriched, and made accurate, but also a number of comprehensive and fertile ideas have been developed one after another, and deductive methods of enquiry made possible, and found to be exceptionally fruitful; chemistry has, in fact, thrown off much of its empirical character, and established itself to be a truly rational science. The educational value which it has thus acquired is enormous, a student of modern chemistry having ample opportunities of cultivating the power of observation, and the faculty of reasoning at the same time. Neither an essentially descriptive science, such as mineralogy, botany, or zoology, on the one hand, nor an essentially abstract science, such as mathematics or logic, on the other, possesses in itself this two-sided advantage. Physics is the only science which, for years, has enjoyed that privilege, but now chemistry has come forward, combining, as it does, experimental and deductive methods of study in due proportion; and its educational value must be regarded as even greater than that of the sister science, for the field of investigation, which a student of modern chemistry has at his command, is more extended and more fertile than that presented to a student of physics. It is more extended because many of the processes going on around us are of the chemical nature, and it is more fertile, because much of it has been left uncultivated or only imperfectly cultivated from want of the requisite means now supplied.

Not only is modern chemistry a keen weapon of sound and scientific education for those who would become pure chemists, but also for those who would have to apply the knowledge of that science in special directions, such as physiology and chemical technology, inasmuch as its conceptions are exceedingly comprehensive and fruitful, and have not only found their applications in these directions, but have also already led to some important practical results.

For boys in secondary schools, teaching of chemistry from the point of view recently attained is no less important, as it puts the most important facts of the science in a clear, intelligent, and rational form, supplying requisite food for the healthy development of their brain.

* Read before the British Association (Section B), Glasgow Meeting, 1901.

Notwithstanding these evident and exceptional advantages which the teaching of modern chemistry affords, it is still taught, to a great extent, in the same dry and merely descriptive way as in old days, explanations which are in direct opposition to well established facts being, moreover, not unfrequently given. Neither repetition of names, formulæ, preparations, properties, and so forth, and description of other isolated facts, nor even exercise in qualitative and quantitative analysis, can be regarded as a source of much mental satisfaction to the student, capable of vigorous, or even moderate, exercise of the mind; and little or no opportunity being given of satisfying his mental aptitude, he may think chemistry a very uninteresting subject, and turn away from it. It is, I think, both possible and probable that we are in this way discouraging some of the brightest students from coming to us, or losing them from among us. At any rate it appears to me to be plain that we are not making use of the very keen educational implement which we possess to its best advantage, and for the interest of our science and profession this state of things should be speedily remedied.

Granting, then, that the present system of teaching chemistry is inefficient and unsatisfactory, and that a more free and general introduction of modern views and methods into it is necessary, I would venture to make a few suggestions for the remedy.

One of the remedies would, I think, be to remove certain misconceptions which seem to prevail pretty freely. Now, the means by which the recent marvellous development has been achieved—a development almost unparalleled in its magnitude and importance in the history of chemistry—is essentially what is called "physical," and, as a consequence of this, what I consider to be a misleading and unfortunate name, that of physical chemistry, has come into general use. It is misleading, because to those who have not watched the progress with special interest, the analogy in name of physical chemistry with physiological chemistry or agricultural chemistry may suggest an idea that it is only a special branch of chemistry. To such an audience as I have now the honour of addressing it is scarcely necessary for me to say that such an idea is entirely mistaken. Whilst physiological or agricultural chemistry applies chemical methods to questions essentially physiological or agricultural, the so-called physical chemistry pervades the whole domain of our science, and treats of chemical problems which are specially fundamental and important, only the methods of research and the instruments employed are mostly those hitherto exclusively used by physicists. These methods and instruments are, however, no longer merely physical, but are also chemical; the determination of electrolytic resistance, for example, is now as much a chemical operation as weighing or measuring, and a galvanometer as much a chemical apparatus as a balance or a litre flask. The name of physical chemistry is not only misleading but also unfortunate, because on account largely of the above misconception, as I take it, not only its cultivation but also its teaching has been much neglected. I would therefore suggest that the name *General Chemistry* should exclusively be used in its stead. Many of you would, no doubt, think this a very trifling matter, and ask, "What's in a name?" but I think there is a great deal in a name, especially as in this case, when it is misleading and liable to hinder progress. Ostwald was perfectly right when he gave the title "Allgemeine Chemie" to his *Lehrbuch*, but I think he made a regrettable mistake in calling that important periodical, edited by himself and van 't Hoff, *Zeitschrift für Physikalische Chemie*.

Another misconception, which seems to have crept into the minds of many, and which has also apparently prevented a more rapid diffusion of modern ideas, relates to the use of mathematics. It is very often stated that as the treatment of general chemistry requires higher mathematics, it is neither possible nor desirable to introduce it into elementary teaching, but it appears to me that in this opinion there is a confusion of ideas. It is true that for a detailed study and cultivation of general chemistry, a fair knowledge of higher mathematics is both desirable and necessary, and I think it well that this fact should be clearly and generally recognised, and that students of chemistry should be encouraged to acquire this knowledge, preferably from a physicist or a chemist rather than from a pure mathematician. But the teachings of general chemistry can be introduced into elementary text-books without any mathematics, save perhaps a few of the simplest algebraic formulæ, and yet in a concise, useful, and interesting form; moreover, simple and appropriate lecture experiments, illustrating the laws of chemical dynamics or the theory of solutions, can be easily contrived. As a means of diffusing the knowledge of, and increasing the interest in, general chemistry, I would therefore suggest that, for the sake of school teachers, courses of lectures in which general chemistry is amalgamated with descriptive matter should be given, say during the summer vacations, and that also writing of elementary text books on the same plan should be encouraged.

There is another point which I wish to mention. The attempt to give a fair training in general chemistry over and beyond what the student has been accustomed to learn would no doubt take up too much of his, as well as of the teacher's time, but I believe that some portions, and even a great deal of the descriptive matter usually given in lectures can be cut off, not with inconvenience but rather with advantage, because in the class-room the attention of students should be more directed to points of general importance and interest, leaving details to be read up by them, and that the time usually devoted to analytical work in the laboratory may also be conveniently shortened, because what the student should learn from it is rather principles and methods of analysis than mere practical skill. Chemical laboratories of universities, and even of colleges, should be institutions which contribute to the sum total of our knowledge, and in which men are trained with that object in view, and not mere workshops for apprentices.

Before concluding, I wish to draw your attention to yet another point, a point which lies on a somewhat different line of thought, but still connected with the question of chemical education. You are, no doubt, aware that an International Committee on Atomic Weights was organised a year or two ago, on the invitation of the German Chemical Society, and with the view of settling upon atomic weights for ordinary use, and that as the standard atomic weight O = 16·00 was adopted by a very large majority. There are, as is well known, many and strong reasons for adopting this standard; yet it appears that outside the International Committee there were several chemists who preferred the standard H = 1·00, and on whose account the German Committee was led to publish two tables of atomic weights, one on the oxygen standard and called "International Atomic Weights," and the other on the hydrogen standard, and called "Dydactic Atomic Weights." Pedagogic reasons seem to be the chief ground of their giving prefence to the hydrogen standard, but I must confess that I am unable to see why. If in teaching chemistry atomic weight is treated before molecular weight, if the student is to be told that the molecular weight of a substance is obtained by summing up the atomic weights of the constituent elements, and if he is made to believe that an atom of such and such an element is so many times heavier than that of hydrogen; if, in short, the most important stoichiometrical laws of chemistry are to be put in the background, then I can understand that there is a preference to the hydrogen standard, but it appears to me that such a method of teaching is a gross mistake, taking the student a century back, and putting him in the same difficulty as Dalton was placed, a difficulty which took fifty years of progress to remove. Now, what are atomic weights, and how are they determined? If, for example, we wish to determine

the atomic weight of carbon, have we not, first of all, to ascertain the molecular weights of as many of its compounds as available? Have we not then to determine the quantities of carbon contained in one molecular weight of each of these compounds? And do we not finally regard the greatest common factor among the numbers, representing these quantities of carbon, as its atomic weight? The very nature of the constants which we call atomic weights requires them to be determined after molecular weights, and it is essential, therefore, that we should first agree upon some one molecular weight as the standard of comparison. Now, in fixing this standard of molecular weight I do not see any better pedagogic reasons for adopting hydrogen and calling its molecular weight 2, than adopting oxygen and calling its molecular weight 32, nor do I see any advantage in defining the common unit of atomic and molecular weights as $\frac{1}{2}$ of the molecular weight of hydrogen, over defining it as $\frac{1}{32}$ of the molecular weight of oxygen. The question simply lies between the two numbers, 2 and 32, both of which are arbitrary, and either of which serves to express with equal clearness the stoichiometrical relations of hydrogen or oxygen to other substances. Looked at and taught from this point of view, as, I think they should be, the quantitative laws of chemical combination do not give preference to the hydrogen standard for their elucidation and illustration; on the contrary, its formal adoption is liable to increase the tendency, already too great, of giving to students erroneous notions on atomic and molecular weights, and of making them think that hypotheses are statements of facts. At the same time, atomic-molecular hypothesis has nothing to lose from the adoption of the oxygen standard. It appears to me therefore that pedagogic reasons go against the adoption of the hydrogen standard, rather than for it.

CONTRIBUTIONS TO THE SCIENCE OF THE NITROCELLULOSES.*

By G. LUNGE and J. BEBIE.

(Continued from p. 145).

In order to obtain more exact conclusions with regard to the stability of gun-cotton we next investigated the effect of treating successively with cold, running, and hot water.

In the first experiment the gun-cotton was treated for three days with cold water. It was placed in a large porcelain dish, which was supplied hourly with fresh water, the nitration product being at the same time well pressed on the vacuum pump. After this followed a similar treatment for two days with hot water (90—93°). One-half was then dried in a dry current of air at 40°, the other in the vacuum desiccator over sulphuric acid. The latter reacted with the "Abel test" at 70° after 4' 15", the former after 2' 1". The stability was therefore quite insufficient. According to Thomas, the Abel test when compared with his own sometimes gives directly contradictory results; accordingly we wished to see how this product would behave towards Thomas's test. Two samples each of 1·2 grm. were placed in an oil-bath furnished with a temperature regulator, and slowly warmed up. After about half-an-hour a violent explosion occurred, which shattered the apparatus. The temperature cannot have been above 100°, for 92° was noted just before the explosion occurred. In this case, therefore, the agreement with the result of the Abel test was only too apparent. Hence, for products of which great stability is not to be expected, the test proposed by Thomas is not to be recommended, having regard to the safety of the experimenter.

In a second experiment, the product was treated, in the way described above, for one day with cold water, three days with hot water, and finally three days more with running water; but here also a sufficiently stable product was not obtained. The Abel test gave 4—6 minutes.

A continuous rotation of the gun-cotton during the washing in running water did not serve materially to improve the results.

The nitration product was now, in a further experiment, washed in a manner similar to experiment 2. After this, seven days' treatment with cold, hot, and running water, there can only remain small traces of residual acids. If the stability were really alone dependent on the removal of these last traces of acid, it would be possible to increase it considerably by neutralisation of the same. The alleged cause of the difficulty of removing the final traces of acid is that the nitration mixture penetrates the innermost cells and particles of the cotton; but if we now finally treat with dilute alkali there is no obvious reason why the latter should not penetrate into the cells with equal facility. Hence, after the above-mentioned seven days' treatment, the product was treated one day longer with hot water, with the addition of 0·2 c.c. N/10 soda solution. The water was still alkaline at the end; it may therefore be safely concluded that there was no longer any acid present; yet the Abel test gave eight minutes only, which still showed insufficient stability. Thus, for improvement beyond these limits, it was necessary to take a fresh starting-point, dependent on other causes. The opinion has already been given that one of these causes may be the presence of foreign matters in the gun-cotton. These might arise from the action of the nitration mixtures on the impurities contained in the cellulose, or they might be ascribed to secondary actions of the acid mixtures on the cellulose itself. Lenk and Cross have recently published a research on this point. They succeeded, by treating with acetone so dilute that it had no solvent action on the gun-cotton itself, in extracting a small quantity of foreign matter, and by this means the stability was considerably increased. This body, which lowers the stability, has not yet been further examined; it contains 9—12 per cent nitrogen. In this way better results should be obtained than by prolonged boiling. It may here be mentioned that, simply by means of boiling for three days, we obtained a stability of more than fifty minutes. The maximum from Cross's experiment was fifty-five minutes. It is an established fact that by boiling for a relatively short time the stability is considerably more increased than by lengthened treatment with cold and hot water.

In all succeeding experiments we proceeded as follows:—After removing most of the adherent nitration acid with cold water the gun-cotton was cut up as finely as possible with scissors, and then boiled with frequent changes of water. In this manner a fairly high stability is obtained in three to four days. It is, as already remarked, unlikely that this result is entirely dependent on the removal of all traces of acid. "Chemically pure bandage wadding" was always used, so it is only conceivable that there may be a secondary action of the nitration mixtures on the cellulose itself.

The stability cannot upon these lines be increased beyond a certain limit. An absolutely stable body is not obtainable, for gun-cotton is in itself an unstable product.

Spica has shown that even the most carefully purified gun-cotton decomposes to a slight extent.

A distinction might therefore be made between a temporary instability caused on the one hand by traces of residual nitration acids, and on the other hand by the presence of foreign matter, and a permanent instability due to the nature of the nitrocellulose molecules.

(To be continued).

* *Zeitschrift fur Angewandte Chemie*, 1901, Heft 20.

Society of Arts Examinations, 1902.—The Programme for 1902 is now ready, and may be had (price 3d., post free) on application to the Secretary, Adelphi, London, W.C. The Examinations will commence on Monday, April 14th, and will be concluded on Thursday, April 17th.

SOME REMARKS ON THE PLACE OF HYDROGEN IN THE PERIODIC SYSTEM.

By GEOFFREY MARTIN.

Hydrogen for many years has been associated with the alkali metals in the periodic arrangement of the elements. The fact which weighed most in attributing such a position to this remarkable element was the undoubted metallic properties it displays when it enters into the composition of acids and salts. In such bodies we find metals and hydrogen are capable of mutually replacing each other; the acids, in fact, may be regarded as hydrogen salts.

The analogies between hydrogen and the metals are too well known to be discussed here.

Of recent years, however, many eminent chemists have expressed doubt as to the advisability of placing it at the head of the alkali metal group.

Some have even suggested a position at the head of the chlorine group of elements (Crookes, *Proc. Roy. Soc.* 1898, 408; Masson, Chem. News, 1896, lxxiii., 283).

The cause which has undoubtedly led to such a revulsion of feeling may be traced to Graham's unfortunate interpretation of the remarkable power which Pd has of occluding it. He believed a Pd-H alloy was formed. It has since been proved that in general hydrides of the various metals have anything but metallic characteristics. LiH and CuH, for example, are respectively white saline and brown powders, quite different in character to alloys.

Graham believed H to be a light volatile metal, while Dewar has proved it to be a colourless liquid resembling strongly a liquid hydrocarbon like CH_4. Liquid hydrogen, in fact, is devoid of metallic properties of any description.

Two main objections have been raised against the position given to H as the first element of the alkali metal group, viz.:—

(1). Hydrogen itself has no metallic characters; therefore it cannot belong to Group I.

(2). The atomic weight of hydrogen is incompatible with such a place; for (*a*) the difference between the atomic weights of H and Li is only 6, while the difference between the elements of series 2 and 3 of Mendeleeff's table averages 15 to 20. (*b*) The position of hydrogen at the head of the alkali metals will necessitate six gaps for undiscovered elements between H = 1 and He = 4.

The following periodic table shows this:—

Periodic Table.

Series.								
1.	H 1	*	*	*	*	*	*	He 4
2.	Li 7	Be 9	B 11	C 12	N 14	O 16	F 19	Ne 20
3.	Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35·5	Ar 40
4.	K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 54	

(1). The first objection includes all those arguments based upon the absence of metallic characteristics, such as the fact that hydrogen does not form alloys, or the fact that the H molecule is composed of two atoms (like the halogens), while metals generally, including the alkali metals, are non-atomic, both in the gaseous and dissolved condition.

All such objections arise out of, and vanish with, the assumption that if H belongs to Group I. it must have metallic properties—an unnecessary and unjustifiable assumption; for while most of the groups of the periodic table begin with non-metallic elements, the heavier elements of the same groups are undoubted metals; increase of atomic weight invariably brings out metallic properties.

For example, carbon and nitrogen are without doubt non-metals; nevertheless, tin and lead of the one group, and antimony and bismuth of the other, are metals. In considering the relation hydrogen bears to the alkali metals it must be remembered that Li has an atomic weight seven times that of hydrogen. It is not, therefore, surprising that while H has no metallic properties Li should be a pronounced metal. In Group III., for example, boron is a pronounced non-metal; nevertheless, the next group element to it—aluminium—with an atomic weight less than three times that of boron, is a most decided metal. Again, in Group IV., titanium with an atomic weight only four times that of the emphatic non-metal carbon exhibits metallic characteristics. Many other examples could be given. The fact that hydrogen itself is devoid of metallic characteristics has, therefore, little weight as an argument for rejecting it from Group I. Its atomic weight is much too low for it to individually exhibit a metallic character in its *physical characteristics*.

On the other hand, in its chemical properties it foreshadows strongly the coming metallic properties of the succeeding heavier elements of the group.

Indeed, as a rule, the chemical characteristics of an element are far surer indications of its analogy to other elements of the same group than are its individual physical properties. Thus, while the gaseous nitrogen is as unlike as can be physically to As or Sb, nevertheless such elements produce compounds which resemble each other to a truly startling degree. Indeed, one could hardly believe that such dissimilar bodies as N, P, As, and Sb could produce such similar compounds as $N.Et_4OH$, $P.Et_4.OH$, $As.Et_4OH$, and $SbEt_4OH$.

With decreasing atomic weight a chemical similarity or behaviour lingers among elements of any one group long after all physical resemblance has disappeared.

The fact that hydrogen still plays its part as a metal in acids and electrolytes generally may be taken as an illustration of this property in the alkali metal group.

(2). We will now proceed to deal with the second objection. (*a*) It is true that the difference between the atomic weights of Li and H is 6, while the differences between the elements Na and K, Be and Mg, B and Al,

&c., average 15—20. But this is, so to speak, a mere local effect depending on the fact that we are *subtracting* atomic weights. If we *divide* them instead we will actually get evidence in favour of the position of H at the head of the alkali metals.

Thus we have :—

$$\frac{K}{Na} = \frac{39{\cdot}1}{23} = 1{\cdot}7,$$

$$\frac{Na}{Li} = \frac{23}{7} = 3{\cdot}3,$$

i.e., the ratios are in the one case nearly double that in the other. If we imagine a similar relation holds for the next ratio between Li and the element above it we have :—

$$\frac{Li}{H} = 3{\cdot}3 \times 2 = 6{\cdot}6.$$

The actual ratio, $\frac{Li}{H} = 7$, is close to this.

It is thus seen that a different way of manipulating the atomic weights leads to quite different results.

We have *à priori* as much right to use the one method as we have to use the other, and the conclusions deducible from the one method have an importance equal to those deducible from the other.

Thus, the objection to the position of H in Group I. on account of the value of its atomic weight falls completely to the ground.

(*b*) The position of H at the head of the alkali metals will necessitate six gaps for undiscovered elements. This has been urged as an objection (Masson, *loc. cit.*).

We have not the slightest reason for doubting the existence of such elements. The mere fact they have not been yet isolated counts for little. With the new horizon that has opened out with the discovery within the last few years of some nine or ten new elements—some such as argon occurring in quite appreciable quantity—indicates the probability that with more refined and at present unknown methods of research will lead to the discovery of many other elements. For example, the Curies, by working with the electrometer as a chemist works with a balance, have discovered several heavy radio-active elements.

We may therefore conclude that, not only does hydrogen find its true place at the head of the alkali metals, but also that the arguments urged against such a position when examined are found to be devoid of weight.

Professor Orme Masson (Chem. News, lxxiii., 283), has put forward the following arguments for attributing to hydrogen a position as the first member of the halogen group of elements. The matter is of some importance, for two famous English chemists seem to have given their adherence to this view (Crookes, *Proc. Roy. Soc.*, 1898, 405; Ramsay, *Proc. Roy. Soc.*, January 8th, 1901). We will deal with Masson's arguments in detail :—

1. *The atomicity of hydrogen* (H_2) *is the same as that of the halogens; so far as evidence goes the alkali metals are, on the contrary, monatomic in the gaseous and dissolved conditions.* This difficulty vanishes if we give up the view that hydrogen is a metal. Even at its best the argument is of doubtful weight in adjudicating a position in the periodic table; for instance, while the N molecule is N_2 the P molecule is P_4, yet both elements undoubtedly belong to the same group.

2. *The gaseous character of hydrogen agrees with a position at the head of the halogen group.* On the other hand, it can be argued that the exceeding lightness of the H molecule is a powerful factor in causing it to be gaseous.

It must be remembered that if H be given a position at the head of the alkali group, Li is seven times as heavy as it. P, which is only a little more than twice as heavy as N, is a solid at ordinary temperatures, while nitrogen is one of the so-called "permanent" gases. The same is true for oxygen and sulphur. It is therefore scarcely surprising that *Li* with an atom seven times as heavy as that of H should be a solid, while H is a very volatile gas.

3. *The evidence which can be drawn from the atom weight of hydrogen favours a position in the chlorine group.* We have discussed this point, and have shown the facts can be interpreted as an argument for a position in Group. I.

4. *In hydrocarbons and other organic compounds hydrogen and the halogens can mutually replace each other, often with no more effect on the general properties of a compound than is produced by the substitution of one halogen for another.* This is to some extent true, but is merely an example of a principle which has been known for many years. According to Laurent and Gerhardt the characteristic properties of a compound depend more upon the way in which the constituent atoms are arranged in the molecule than upon the chemical nature of the atoms themselves, so much so that even if the most diverse radicals entered into a compound by displacing another radicle they would, in virtue of their position in the molecule, continue to perform the function of the displaced radicle, and thus would not materially alter the fundamental characteristics of the body into which they entered.

It is thus seen that little can be said in favour of placing hydrogen at the head of the halogen group of elements. On the other hand, the following arguments are in direct opposition to such a view :—

(1). If we consider the capability of the elements I, Br, Cl, and F to combine with oxygen, we find that, while the oxides of iodine are, comparatively speaking, stable, the oxides of Br and Cl are much more unstable, and decompose explosively on the slightest provocation, while the oxide of F appears to be too unstable to exist. It is clear, therefore, that as the atomic weight decreases from iodine downwards in the halogen group, the capacity for combining with oxygen decreases, until finally F refuses altogether to form an oxide. If hydrogen was really a member of this group, with an atomic weight lower than F, we should expect it to absolutely refuse to combine at all with oxygen.

As a matter of fact H does unite with oxygen with great energy to form water—a most stable substance totally unlike the unstable oxides of the halides.

(2). The halogens combine energetically with Na at ordinary temperatures, with the evolution of great heat. H, however, shows but little affinity for the alkali metals, and usually requires to be heated before a noticeable amount of combination occurs. Further, such hydrides are most unstable bodies (*e.g.*, Cu_2H_2)—for instance, when NaH is treated with Hg, the Na and the Hg unite, and hydrogen is expelled—a behaviour totally different from the stable halides of the alkali metals.

It is needless to give any other examples. They can be multiplied indefinitely.

Indeed, the entire chemical behaviour of hydrogen and its compounds most decisively shows it has utterly nothing in common with the halogens.

On the other hand, the compounds of H call to mind the compounds of the alkali metals.

Its chloride is a stable body formed with evolution of heat and light; its oxides resemble those of the alkalis; H_2O resembles KHO, and acts as a feeble base. For example, both H_2O and KHO are capable of causing hydrolysis, while H_2O_2 is analogous to the peroxides of sodium and potassium. Hydrogen also forms sulphates, nitrates, oxalates, &c., all analogous to similar compounds of the metals.

There is thus a very real analogy between the compounds of H and those of the alkali metals.

Bristol, September 1, 1901.

Generator Gases produced by means of "Linde" Air.—The Verein zür Beförderung des Gewerbefleisses in Berlin has offered a prize of £150 (3000 marks) and the large gold medal for the best work on the results of experiments with generator gases, produced by concentrated oxygen ("Linde" air). The work must be given in by November next.

ELECTROLYSIS IN BLEACHING TEXTILES.

The application of electricity to manufacturing processes has long occupied the attention of scientific men and inventors. Every effort has been made in recent years to simplify and cheapen the cost, not only of the necessary machinery, but of chemical elements as well. Some Germans have invented an apparatus for producing "chemic," or bleaching liquor, out of ordinary brine, the product being sodium hypochlorite, which is attracting considerable attention among textile manufacturers on the Continent. It is claimed that the chemic obtained by this method produces a whiteness superior to that of the ordinary English bleaching liquor.

The following detailed description of the invention and its improvements may be of interest to the textile manufacturers of the United Kingdom :—

The ordinary apparatus is extremely simple, being mainly a trough or box of slate, swung on trunnions, in a suitable frame, with an inlet for the brine, and an outlet for the sodium hypochlorite resulting from the passage of a current of electricity through the brine as it runs through the box, the poles or electrodes being placed at opposite ends of the box.

Thermometers are suspended at the inlet and at the outlet in order to show at a glance the strength of the sodium hypochlorite, it having been found that every rise of 5° C. corresponds to 1 grm. of free or active chlorine per litre (equal to 62 grains per gallon).

In order to clean the apparatus the thermometers are removed, and the trough reversed and cleansed with a hose-pipe. The electrodes last about one year, and can be easily replaced. The bleaching liquor, the product of the apparatus, is suitable for bleaching raw cotton, yarn, cloth, lace, and embroidered fabrics made of cotton, linen, jute or flax, pulp, paper, &c. It advantageously replaces chloride of lime for these purposes.

The advantages claimed for this system are :—

1. The electrolysed solution possesses high decolorising or bleaching power.

2. The goods treated in the ordinary process of bleaching are not harmed, and there is scarcely any appreciable loss in weight.

3. Lime or magnesia salts are not deposited on the cloth, thereby eliminating trouble in subsequent dyeing and printing.

4. Constant strength of liquor, which can be used as fast as made, if desired.

5. Economy in cost of production.

The apparatus is constructed in three sizes, to produce per ten hours respectively, 350, 650, and 1000 gallons of electrolysed solution, containing 3 grms. per litre (equal to 186 grains per gallon), of active chlorine, prepared from brine of a strength of 6° Baumé.

For purposes of comparison we may say that 650 gallons of the electrolysed solution contain 20 pounds of active chlorine; to obtain from chloride of lime 20 pounds of active chlorine it would be necessary to use 70 pounds of bleaching-powder, and the resulting 650 gallons would be found to give inferior results. The reason of this difference lies in the constitution of the electrolysed liquor, which has been found to contain the following :—Free chlorine, free hypochlorous acid, sodium hypochlorite, and sodium chlorate. It is chiefly the free hypochlorous acid which causes the rapid bleach. This solution is harmless to the fibres of the threads—the best proof that they are not injured being that goods bleached by electrolysis only lose about 2 per cent, as against some 8 per cent for chloride of lime bleach.

When making further comparisons between the new and the old methods, it is well to bear in mind the fact that chloride of lime quickly loses its strength. It is invariably assumed to be of some given standard, but as the hydrometer test is deceptive and other tests are troublesome, guessing is generally resorted to, and cloth is often spoiled. In this apparatus the difference between the readings of the two thermometers is a ready and infallible test, though that is scarcely needed after once regulating the flow of the brine and the electrical current. The electrolysed liquor is always of one strength; mixing or reducing is not necessary, neither does the apparatus need attention. Rock-salt or sea-salt may be used in addition to waste salt for mixing brine, provided it contains no minerals injurious to the subsequent processes.

Another apparatus produces a liquid six times stronger, intended for use in steam laundries.

All the apparatuses can be connected with a dynamo already in use for electric lighting, or any other electrical source of supply.

For further particulars apply to W. R. B. Lockie, 17A, South Castle Street, Liverpool, Agent for Great Britain.

THE SOLUBILITY OF MANGANOUS SULPHATE.*

By THEODORE WILLIAM RICHARDS
and
FRANK ROY FRAPRIE.

The solubility of manganous sulphate has been carefully determined within the past year by F. G. Cottrell (*Journ. Phys. Chem.*, 1900, iv., 637), and the present paper is written to confirm in some measure the results of his work. He was able to disprove, by well considered experiment, the less recent work of Linebarger (*Am. Chem. Journ.*, 1893, xv., 225), who published a singular series of results resting upon faulty reasoning and an erroneous method of experimentation. In a case of this kind, when authorities differ, the truth is more quickly acknowledged when it is supported, hence the publication of the present paper.

The work to be recorded below was done in the spring of 1898, long before the work of Cottrell. It was part of a still unfinished investigation which has as its object the study of the transition equilibria of potassic manganous sulphate. We hope that circumstances may permit the early publication of the remainder of this work, which has been suspended for a time. (A brief statement of the scope and object of this work will be found in *Proc. Amer. Assoc. Adv. Sci.*, 1898, 213).

It was soon found that a much higher temperature was necessary to drive off the water of crystallisation of manganous sulphate than has usually been supposed. Linebarger used only 180°, at which temperature at least one molecule of water remains in the salt if it is surrounded by air with the usual proportion of aqueous vapour. The handbooks name 210° to 240° as the temperature required, and Cottrell, calling attention to Linebarger's error, used 280°. We found that traces of water still remained after heating for half-an-hour at 350° in an air-bath. In this respect the substance reminds one of cupric sulphate (Richards, *Proc. Amer. Acad.*, 1891, xxvi., 240). The amount thus retained does not much exceed the tenth of a per cent, and the effect upon Cottrell's results could not have been serious. On the other hand, a temperature just below redness, perhaps 450°, obtained with a carefully watched naked flame, and applied after drying at lower temperature, was capable of driving off in five minutes so much of the water that subsequent similar heating for a quarter of an hour showed only an average loss of 0·2 m.grm. The product was wholly soluble in water, showing that no decomposition of the sulphate itself had occurred.

The manganous sulphate was purified with great care, and the crystals employed were coarsely powdered. The specimen whose solubility was to be determined was put into a large stout test-tube with a carefully cleaned rubber stopper, and was kept for at least four hours at the desired temperature in an Ostwald thermostat before a

* Presented to the American Academy of Arts and Sciences, March 13, 1901. From the *American Chemical Journal*, xxvi, No. 1.

sample was taken. The agitation of the mixture was active and continual, being effected by an apparatus similar in principle to that of Schröder (Schroder, *Zeit. Phys. Chem.*, 1893, xi., 454; Noyes, *Ibid.*, 1892, ix., 606; for details see Richards and Faber, *Am. Chem. Journ.*, 1899, xxi., 168, and Chemical News, xxix., 198). The motive power was a Henrici hot-air motor. At the close of the appointed time the sample to be analysed was removed by an effectual filtering pipette, somewhat similar to one which has since been used in van 't Hoff's laboratory (van 't Hoff and Meyerhoffer, *Zeit. Phys. Chem.*, 1898, xxvii., 79). A diagram of the pipette is appended. The

Filtering Pipette.
The filtering attachment, filled with cotton-wool ("absorbent cotton," c), is temporarily attached to the jet, A, of a 5 c.c. pipette by means of the rubber tube, B.

cotton was necessary to filter off the fine powder which appeared during the stirring. In order to avoid change of temperature, the pipette was previously warmed by placing it in a dry test-tube immersed in the thermostat. Only the mouth of the test-tube was allowed to project above the water of the thermostat, and of course every precaution was taken to obtain a fair sample of the solution.

After filling the pipette and quickly removing the rubber filtering-jet attached to it, the clear solution was run into a weighing-bottle and was quickly stoppered and weighed. The known amount of solution was washed into a roomy platinum crucible, when it was cautiously evaporated, and the residue was ignited in the fashion already described. In order to make certain that no transition had occurred during the experiment, the crystal water contained in the solid phase left over after the saturation was always determined. Below are the data thus obtained:—

The Solubility of $MnSO_4.5H_2O$ *at* 25°.

No. of determination.	Time of saturation. Hours.	Weight of solution. Grms.	Weight of $MnSO_4$. Grms.	$MnSO_4$ for 100 grms. water. Grms.
1.	6	5·0342	1·9849	65·09
2.	6	6·3405	2·4947	64·89
3.	8	4·4318	1·7470	65·07
4.	8	5·2465	2·0656	64·94
		Average..		64 99
5.	48	3·4514	1·3622	65·20
6.	72	3·5349	1·3947	65·17
		Average..		65·19

Cottrell found 64·78 as a mean of two closely agreeing determinations, but the time allowed for saturation was only two and one-fifth hours. The probable reason for his slightly lower result will be discussed below.

The solubility of the tetrahydrate is recorded below:—

The Solubility of $MnSO_4\ 4H_2O$ *at* 30·15° *and* 35·0°.

No. of determination.	Temperature.	Time of saturation. Hours.	Weight of solution. Grms.	Weight of $MnSO_4$. Grms.	$MnSO_4$ for 100 grms. water.
7.	30·15°	4	4·3125	1·7215	66·44
8.	30·15°	4	5·7567	2·2943	66·27
9.	30·15°	4	4·5992	1·8339	66·32
10.	30·15°	4	5·2322	2·0894	66·48
			Average..		66·38
11.	35·0°	13	3·7009	1·5007	68·21
12.	35·0°	14·5	2·7854	1·1296	68·22
			Average..		68·22

The solid material taken from the tubes in Determinations 7 to 10 contained as much as 4·3 molecules of water for each $MnSO_4$, but it was, nevertheless, probably the designated hydrate containing included mother liquor. The greater solubility of the pentahydrate at 30° would certainly involve the solution of any accessible pentahydrate. The salt remaining from Determinations 11 and 12 contained 4·03 molecules of water.

The results at 30·15°, giving an average of 66·38, correspond almost exactly with Cottrell's figure, 66·43 at 30°; but in this case his time of saturation was increased to an average of three hours, while ours was not much longer. Hence close correspondence was to have been expected, and the figures mutually support one another. The slight difference may be due to a residual trace of water in Cottrell's salt.

On the other hand, at 35° Cottrell used only two hours for saturation, while we used about seven times as much time. Hence the difference between his result, 67·87, and ours, 68·22, may be explained once more by a difference in the time of mixing.

Until recently the cause of this difference would have been ascribed to a possible incomplete saturation in Cottrell's case; and the higher figures, other things being equal, would have been accepted as the more accurate.

While this may be true, the recent work of Ostwald (*Zeit. Phys. Chem.*, 1900, xxxiv., 495) on the solubility of powders and the surface-tension of solids has thrown new light on this matter, and it seems quite possible that neither series of results may be perfectly definite. Fine powders have a greater solution-tension than coarse ones, for the same reason that small drops have a greater vapour-tension than large ones.

It has often been stated that very long agitation is necessary to secure saturation (for example, see "Ostwald's Physico-chemical Measurements," Walker, Macmillan, 1894, p. 176). In view of Ostwald's newer work, it seems quite possible that continued active agitation introduces an uncertainty even greater than the one which it avoids. The crystals of salt in the ever-moving tube act as mutual millstones, and gradually wear off one another's corners, with the production of fine powder. This fine powder must continually dissolve, because it is more soluble than the larger aggregations. At first it would simply hasten the speed of attaining saturation; but later, when saturation with respect to the larger particles has been attained, the fine powder will tend to produce a solution supersaturated with respect to those larger particles. The experience of Cottrell and others seems to indicate that supersaturation is harder to obviate than inadequate saturation. Cottrell, for example, found that $MnSO_4.H_2O$ attained a concentration of 57·41 grms. in 100 grms. of water after two hours of agitation when the salt was added to pure water, while after twice as long a time the supersaturation in another tube had only been reduced from 72·5 to 62·3

grms. per 100. The solubility found after twenty-seven hours, when both methods gave the same result, was 58·32, or 0·91 grm. more than the first and 4 grms. less than the second figure.

The outcome of the matter seems to be that constant results upon solubility are usually obtained only when the rate of production of the fine powder exactly balances the rate at which the supersaturation is relieved, and that constant results thus reached represent only a compromise. With cautious agitation, it is possible that a solubility very near that of flat crystal surfaces might be obtained; on the other hand, very active agitation, such as we used, must tend to increase this solubility almost to that corresponding to the fine powder which we always observed in our tubes.

Everyone will agree with Ostwald in deciding that the solution-tension of flat surfaces, rather than that of sharply curved surfaces, is the quantity which should be determined, if possible. This result would be best obtained by keeping the solid as free as possible from agitation, and driving a constant current of the saturating solution over these resting crystals. A dissolving apparatus which has recently been described, if assisted by a small turbine and suitably immersed in a thermostat, would perhaps be the safest apparatus, although complete saturation would require much time (Richards, *Amer. Chem. Journ.*, 1898, xx., 189).

It is evident, as Ostwald points out, that most published determinations of solubility, those of Cottrell and our own included, are subject to a small uncertainty; but it is also evident that the work of Cottrell is by far the most complete work upon the solubility of manganous sulphate which has been published, and that it wholly overthrows the erroneous results of Linebarger.

We determined also the solubility of both the dihydrate and the tetrahydrate of the double sulphate of manganese and potassium, and found solutions saturated at 25° with both or either hydrate to yield 40·1 grms. of anhydrous solid. Hence this temperature must be near the transition temperature of the two hydrates. The detailed publication of these results and many other similar observations must be reserved for a later communication.

In a few words of recapitulation, the present paper may be said to confirm the work of Cottrell and to disprove that of Linebarger, while a measure of doubt is cast upon the usual methods of determining solubility.

THE ESTIMATION OF CARBONIC ACID IN WATER.*

By JOSEPH W. ELLMS and JAY C. BENEKER.

(Continued from p. 146).

Lunge-Trillich or Seyler Method (continued).

THE essential details of the Seyler process are as follows:—

The free carbonic acid is determined by placing 100 c.c. of the sample in a glass cylinder with 25 to 30 drops of a neutral solution of phenolphthalein. To the sample is then added a solution of sodium carbonate (0·05 or 0·02 normal solution may be used), stirring carefully and thoroughly until a faint permanent pink colour is obtained.

The following precautions have been found desirable if accurate results are to be expected:—

1. The titration can conveniently take place in a short Nessler cylinder. The writers used a tube approximately 18 c.m. long by 3 c.m. in diameter, graduated for 50 and 100 c.c. The stirring rod used was bent at its lower end into the form of a circle, and then turned so as to stand at right angles to the rod. A comparison cylinder containing the same amount of water as there was in the titrating cylinder, was found to aid in the determination of the end-point.

2. The larger part of the sodium carbonate solution should be added quickly, and the strong pink colour formed should be discharged by stirring and mixing with the rod. The titration can then be cautiously completed. When the colour remains permanent the titration is complete. The sodium carbonate solution should be prepared with freshly ignited sodium carbonate, and with water which has been thoroughly boiled and cooled out of contact with the air. The exposure of this solution to the air should be avoided as much as possible, as sodium bicarbonate is readily formed, which renders it useless for this titration where accurate results are desired.

3. With waters that are high in free and half-bound carbonic acid it is better to use less than 100 c.c. for the titration, especially if 0·02 normal sodium carbonate solutions are used. With such a water, care is necessary in transferring the sample to the cylinder in order to avoid loss of carbonic acid. Too vigorous stirring of the water is also to be avoided for the same reason.

The fixed carbonic acid, from which the half-bound acid is estimated, is determined according to the method of Hehner. Seyler uses methyl orange as the indicator for this titration, but the writers employed lacmoid. The accuracy of this process (J. W. Ellms, *Journ. Amer. Chem. Soc.*, xxi., 359), is well known, and need not be here discussed.

In the absence of free carbonic acid in a water, the half-bound may equal the fixed, in which case it would be neutral to phenolphthalein. If, however, the water is alkaline to phenolphthalein, the half-bound carbonic acid does not equal the fixed; or, in other words, a portion of the carbonates of the bases exist in solution without the assistance of any half-bound carbonic acid. In such a case the half-bound acid is obtained by first determining the fixed carbonic acid by means of lacmoid. From this is deducted an amount of carbonic acid equal to twice the quantity indicated by the acid required to discharge the pink colour produced by phenolphthalein. The difference is the amount of half-bound carbonic acid which is present. These titrations may be made on the same sample, in which case the "phenolphthalein alkalinity" is first determined, and then followed by the titration with lacmoid; or they may be made on separate samples.

The principles upon which the above procedure is based have been pointed out above.

These titrations involve no especial difficulties, and can be easily and quickly carried out. Approximately 0·02 normal solutions of sulphuric acid were used by the writers and the same strength of sodium carbonate solution. Seyler has prepared a series of formulæ for calculating the results, which simplifies the work somewhat. If results are obtained with 100 c.c. of the sample and the reagents employed are 0·02 normal, the following formulæ express the results in parts per million:—

I. For waters acid or neutral to phenolphthalein:—

Free carbonic acid .. .. $=4{\cdot}4\,p$
Fixed or half-bound carbonic acid.. $=4{\cdot}4\,m$
Volatile carbonic acid .. .. .. $=4{\cdot}4\,(m+p)$
Total carbonic acid .. .. $=4{\cdot}4\,(2m+p)$

p = c.c. 0·02 normal sodium carbonate solution required to produce a pink colour with phenolphthalein in 100 c.c. of the water; and

m = c.c. 0·02 normal sulphuric acid solution required to obtain the end-point with methyl-orange or lacmoid in the same volume of water.

II. For waters alkaline to phenolphthalein:—

Fixed carbonic acid .. .. $=4{\cdot}4\,m$
Half-bound or volatile carbonic acid $=4{\cdot}4\,(m-2p')$
Total carbonic acid .. .. $=4{\cdot}4\,(2m-2p')$

m = c.c. 0·02 normal sulphuric acid solution required to obtain end-point with methyl-orange or lacmoid in 100 c.c. of the sample.

p' = c.c. 0·02 normal sulphuric acid required to discharge the pink colour produced by phenolphthalein in 100 c.c. of the sample.

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* *Journal of the American Chemical Society*, xxiii., No. 6.

There is a third case in which free carbonic acid might exist in a solution containing free mineral acid, and for which Seyler has given a method with its corresponding formulæ for calculating the results. But such a condition would seldom be found in natural waters, and need not here be described.

The errors affecting the accuracy of Seyler's method are those which arise in part from the determination of the free carbonic acid. The end-point in the titration of the sample with sodium carbonate and phenolphthalein is not entirely satisfactory. The results obtained are usually low, but with care and practice the error from this source should be less than 2 to 3 parts per million, even with considerable amounts of carbonic acid, and on small amounts it is less still.

The error due to the determination of the fixed carbonic acid, from which the half-bound is derived, arises from those errors involved in the carrying out of Hehner's method, and which in good work ought not to exceed 1 to 2 parts per million.

(To be continued).

THE DISSOCIATING POWER OF DIFFERENT SOLVENTS.*

(A Summary).

By HARRY C. JONES.

Concluded from p. 146).

Mixed Solvents.

Hydrogen Dioxide and Water.—The dissociating power of a mixture of hydrogen dioxide and water has not yet been measured, but Calvert (*Ann. der Phys.*, i., 483), has found that the dielectric constant of such mixtures is greater than that of pure water. He employed the beautiful method of Drude, and from the dielectric constant of the mixture he calculated the dielectric constant of pure hydrogen dioxide to be 92·8 at 18°. The dielectric constant of pure water at this temperature is, according to Drude, 81.

J. J. Thomson (*Phil. Mag.*, xxxvi., 320), pointed out, as has already been mentioned, that there is probably a very close relation between the dielectric constants of solvents and their dissociating power. We shall see that while the two are not proportional, there is undoubtedly a qualitative relation between them. It is therefore very probable that the dissociating power of hydrogen dioxide is greater than that of water. This would not be very surprising, since many of the properties of hydrogen dioxide are simply the properties of water intensified. Work on this problem is now in progress in this laboratory.

Mixtures of Water and the Alcohols.—A number of experimenters have worked with mixtures of water and one or another of the alcohols. We should mention the work of Lenz (*Mem. de l'Acad. de St. Petersbourg*, [7], xxx., 1881), Stephan (*Wied. Ann.*, xvii., 673), Kerler ("Dissertation," Erlangen, 1884), Kablukoff (*Zeit. Phys. Chem.*, iv., 432), Carrara (*Gazz. Chim. Ital.*, xvi. 1), Schall (*Zeit. Phys. Chem.*, xiv., 701), and Arrhenius (*Zeit. Phys. Chem.*, ix., 487). Quite an elaborate investigation on the conductivity of electrolytes in mixtures of water and ethyl alcohol, was carried out by Wakeman (*Zeit. Phys. Chem.*, xi., 49). His work had to do chiefly with the organic acids in mixtures of these solvents containing varying amounts of alcohol. The results showed that the conductivity became gradually smaller as the amount of alcohol present became larger and larger—just as would be expected from the relative conductivities in these two solvents.

But results of a very different character were obtained by Zelinsky and Krapiwin (*Zeit. Phys. Chem.*, xxi., 35) in mixtures of methyl alcohol and water. It will be remembered that electrolytes in methyl alcohol conduct, in general, to a much smaller degree than in water; yet certain salts were found to have greater conductivity in pure methyl alcohol than in a mixture of 50 per cent methyl alcohol and 50 per cent water. This is shown by the following table, taken from the work of Zelinsky and Krapiwin (*Zeit. Phys. Chem.*, xxi., 49):—

Potassium Bromide.

	Water.	Methyl alcohol.	Methyl alcohol, one-half; water, one-half.
v.	μv.	μv.	μv.
16	123·1	—	59·82
32	127·5	69·02	62·46
64	130·5	76·70	65·36
128	132·9	83·60	67·11
256	136·4	88·96	69·26
512	140·2	93·26	70·53
1024	143·4	97·25	—

Ammonium Iodide.

16	125·4	72·24	62·63
32	129·6	78·74	65·04
64	133·4	85·0	67·48
128	135·9	91·14	69·28
256	138·7	96·20	70·34
512	141·3	100·6	71·12
1024	143·7	104·7	71·57

It is impossible at present to say what these surprising and very remarkable results mean. They are confirmed by the work of Kerler and of Carrara.

Similar results were obtained by Cohen (*Zeit. Phys. Chem.*, xxv., 31) with ethyl alcohol and water, but only when the mixture contained very little water and at dilutions which were quite large, as is shown by the following table:—

Potassium Iodide.

	Pure alcohol.	Eighty parts alcohol and twenty parts water.
v.	μv.	μv.
64	26·1	30·9
128	29·2	32·2
256	31·8	33·2
512	34·4	34·1
1024	36·0	34·5
2048	36·3	35·0

The conductivity in the mixture is the greater until a dilution of 512 litres is reached, when the conductivity in the pure alcohol becomes greater than in the alcohol containing 20 per cent of water.

Cohen found, however, for most substances that the presence of water in the alcohol increased the molecular conductivity, as we would expect.

Conclusions from the Work thus far Done.

An examination of the work described in this review will show that different solvents have very different ionising power. With the possible exception of hydrogen dioxide, water is the strongest ioniser; next to this comes formic acid. Of the more common solvents, methyl alcohol dissociates to a much greater degree than ethyl alcohol. Indeed, it is true, in general, that *in an homologous series of solvents the lower members have the greater dissociating power.*

It has already been mentioned that attempts have been made to discover relations between the ionising power and other properties of a solvent. Thomson's theory that the dissociating power and the dielectric constants of solvents should stand in very close relation to each other, undoubtedly contains a large element of truth. Those solvents which have the largest dissociating power have, in general, the largest dielectric constants. A number of independent investigations have shown that these two properties are not proportional.

* *American Chemical Journal*, xxv., No. 3.

The suggestion of Dutoit and Aston that there is a connection between the amount of association of the molecules of a solvent and its power to ionise electrolytes, undoubtedly contains much truth. Thus, the molecules of water are associated to a greater extent than those of any other liquid, as Ramsay and Shields have shown. The molecule of liquid water at ordinary temperatures is $(H_2O)_4$. Similarly, the alcohols and other strongly dissociating solvents show considerable association of their molecules.

It will probably be shown that the dissociating power of a solvent is not a function of any one physical or chemical property of the substance, but of them all. Or, perhaps, more accurately expressed, all the properties of a substance are a function of the energy relations which obtain in that substance, and ionising power is simply one of these properties.

The conclusion from this work which is of chief importance for pure chemistry is that ions are almost always present when chemical reaction takes place. When the number of solvents which can effect ionisation to some extent is considered, and the fact that heat and possibly pressure can dissociate molecules, it will be seen that there is scarcely a chemical reaction in which ions as well as molecules are not present. The question then arises—Which causes the reaction, the ions or the molecules? This can be answered by excluding ions and then observing whether chemical reaction takes place or not. This has been done, with the following results:—Hydrochloric acid gas, dried and dissolved in dry chloroform, does not conduct the current, and is, therefore, not dissociated. Under such conditions it will not decompose carbonates. Liquid hydrochloric and sulphuric acids, when free from water, will not turn litmus red. Dry hydrochloric acid gas and dry ammonia gas do not react to the slightest extent. Still more surprising perhaps, is the fact that sulphuric acid free from water will not react upon dry metallic sodium. Special precautions must be taken, of course, in all such cases to remove every trace of moisture.

The above examples might be largely increased, but these suffice to show the chemical inertness of molecules. We are now in a position to say that most chemical reactions, if not all, are reactions between ions, and molecules as such do not enter into the reactions at all. As the reactions proceed and the ions already present are used up, the molecules are gradually dissociated and furnish new ions which then enter into the reaction. The chemistry of atoms and molecules has thus given place to the chemistry of ions.

NOTICES OF BOOKS.

Chemical Lecture Experiments. By Frances Gano Benedict, Ph.D., Instructor in Chemistry in Wesleyan University. New York: The Macmillan Company. London: Macmillan and Co. 1901.

The object of this book is to furnish teachers of chemistry with a selection of lecture experiments that can be made quickly, and not needing costly or complicated apparatus. The book will be of value to any who have a number of classes to prepare for, and limited time. It is full of devices for producing striking effects with simple commonplace apparatus. The chapters on the preparation of gases are good, and include many simple though little known methods. In some cases there seems to be a tendency to make rather too much of the *effect*. For instance, to show the combustion of charcoal, finely powdered charcoal is heated to redness, and poured into a jar of oxygen, the hands and face of the operator being protected with gauntlets, &c.!

We are afraid that in this case the truth that it is desired to demonstrate would be swamped in the effect. However, the book does not claim to be a text-book, and the teacher who makes use of it must use his own discretion in selection.

To facilitate the preparation of the experiments a list of chemicals and apparatus required has been appended, in no case demanding anything not ordinarily found on a lecture table. The book is well illustrated and indexed.

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THE CHEMICAL NEWS.

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ON THE CHEMICAL AND BIOLOGICAL CHANGES OCCURRING DURING THE TREATMENT OF SEWAGE BY THE SO-CALLED BACTERIA BEDS.*

By Professor LETTS, D.Sc., Ph.D., and R. F. BLAKE, F.C.S., F.I.C.

IT is generally assumed that the so-called "bacteria beds" act as oxidising agencies absorbing oxygen from the air during their periods of rest, and subsequently transferring it to the constituents of the sewage when the beds are filled with this latter, the transfer being effected by micro-organisms which have established themselves on the surface of the material with which the beds are filled.

It also appears to be generally taken for granted that the micro-organisms mainly concerned in the purification process are the nitrifying organisms. Hence if these views are correct, the effluent from the bacteria beds should contain nitrates and nitrites equivalent in amount to the unoxidised nitrogen which disappears during the treatment. But on examining the results obtained by chemists in investigation on sewage purification it will be found that comparatively small amounts of nitrate and nitrite are produced in relation to the unoxidised nitrogen disappearing.

The following figures are taken (or have been calculated) partly from results given in the Manchester Report of the Rivers Committee, January 22nd, 1900, Table I., the Leeds Report on Sewage Disposal, December, 1898, Table I., and partly from the Table (p. 68), given in Dibdin's book on the "Purification of Sewage and Water."

	Nitrogen disappearing as "free" and "albumenoid" ammonia.	Nitrogen found in the effluent as nitrate and nitrite after double contact with the bacteria beds.	
	Grains per gallon.	Grains per gallon.	Percentage on nitrogen disappearing
Manchester ..	1·634	0·636	39
Sutton	7·185	1·100	15
Leeds	1·528	0·11	7

It is quite evident, therefore, that a considerable portion, and in most cases the greater part, of the unoxidised nitrogen which disappears must be got rid of in some other form, and the question arises as to how this may occur. In all probability there are two—and only two—alternative ways in which the nitrogen can be lost, viz.:—

1. It may escape in the gaseous state as free nitrogen, or possibly as oxides of nitrogen.

2. It may pass into the tissues of animals or vegetables, the former of which may escape from the bacteria beds, and the latter (and possibly the former also) may remain permanently in the beds.

In other words, there may be either a chemical or a biological explanation, or both together.

Chemical Explanation.—In an investigation on the effects of double contact with bacteria beds on screened and settled sewage the authors made analyses of the dissolved gases present, both in the original sewage and in the effluent from both beds, the samples being collected in such a manner that they did not come into contact with the air.

The general results of these analyses were as follows:—1. Practically no oxygen was present, either in the sewage or effluents. 2. The effluent from first contact always contained considerably more carbonic anhydride than the original sewage, and with two exceptions the effluent from second contact also contained an excess of that gas. 3. In eleven out of twelve series of analyses the quantity of nitrogen in the effluent was in excess of that present in the original sewage, and, generally speaking, it was in larger excess in the effluent from double contact than in that from single contact.

As the first six series of analyses only were made under exactly the same conditions, the authors find that, taking them as the basis of calculation, on the average the excess of nitrogen in the effluent from second contact over that present in the sewage amounted in weight to 0·272 part per 100,000, while the loss of unoxidised nitrogen which had occurred in the sewage (by Kjeldahl's process) amounted to 2·2 parts, or that 12 per cent of the nitrogen lost from the sewage during purification was thus accounted for, while in one particular case it amounted to 31 per cent.

In all probability only a fraction of the free nitrogen actually evolved would be retained by the effluent, the rest escaping into the air.

Biological Explanation.—As regards the possibility that nitrogen is lost biologically, *i.e.*, is absorbed into the tissues of animals or plants which feed on the sewage, there can be no doubt that a portion does escape in that way. The bacteria beds at Belfast, and elsewhere, swarm with minute insects (*Podura aquatica*). These, escaping in myriads, often form a thick layer on the surface of the effluent, which looks like soot. There can be no question that in thus escaping these animals carry with them some of the nitrogenous constituents of the sewage which they have devoured, but as yet the authors have formed no estimate of the quantity so removed. There are also species of worms always present in the bacteria beds in considerable numbers which no doubt also feed on the sewage.

* Read before the British Association (Section B), Glasgow Meeting, 1901.

SULPHURIC ACID AS A TYPHOID DISINFECTANT.*

By SAMUEL RIDEAL, D.Sc. (Lond.), F.I.C.

THE comparatively small quantities of sulphuric acid which are necessary to inhibit the growth of *Bacillus typhosus* in water has long been known, and quite recently the author, in conjunction with Dr. Parkes (Parkes and Rideal, *Epidemiological Society's Transactions*, 1901, xx.), has suggested the use of acid sulphate of soda for sterilising potable water amongst armies in the field and for colonists when away from satisfactory water supplies.

The sodium bisulphate is to be preferred for this purpose, as it is more portable than sulphuric acid. Comparative experiments with sodium bisulphate, tartaric acid, citric acid, and nitro-hydrochloric acid and sulphuric acid show that the organic acids are less efficient than the mineral acids for this purpose, and that nitrohydrochloric acid of equal acidity to sulphuric acid is superior, owing no doubt to the fact that the action due to the acid is supplemented by the potential free chlorine that is present in such a mixture.

In our experiments, the following results were obtained:—

750 c.c. of Tap-water Infected with One Drop of a twenty-four hour Broth Culture at 37° C. of Bacillus typhosus.

Agar plate cultures made with 1 c.c. of mixture.	Acidities per pint required to kill, in c.c. N/10 acid.		
	In five minutes.	Fifteen minutes.	Forty-five minutes.
Sodium bisulphate . ..	84	—	42
Tartaric acid	—	86	—
Citric acid	—	203	—
Nitro-hydrochloric acid .	—	31·25	—
Sulphuric acid	—	33	—

* Read before the British Association (Section B), Glasgow Meeting, 1901.

For sterilising water in bulk in case of typhoid outbreak, or in isolation hospitals, sulphuric acid being the cheapest reagent is to be preferred, and possesses advantages over methods of heat sterilisation which lead one to imagine that its more general use for this purpose would be advantageous. The alkalinity of sewages, and that present in most drinking waters, neutralises a certain amount of acid, and therefore an additional amount based upon the alkalinity of the infected water has to be allowed for. It is known, however, that sewages have an alkalinity which seldom falls below 20 parts per 100,000 or rises above 60 parts per 100,000 of sulphuric acid; in other words, the addition of 3 grms. of sulphuric acid per gallon is sufficient for neutralising any possible alkalinity in a sewage or drainage water from an infected area. As the quantity of acid required for inhibiting the growth of the typhoid organism can be taken at 1 grm. per gallon, it follows that an addition of 4 grms. of sulphuric acid per gallon is sufficient for ensuring the death of the typhoid organism in the drainage waters from an isolation hospital or other infected area. It further follows that the free acidity produced in this way would be speedily neutralised when such water becomes mixed with any fresh sewage which has not been similarly treated, and as the infected sewage must always represent a very small proportion of the total drainage to be dealt with, this method of ensuring the absence of typhoid in drainage waters is satisfactory in practice. Although there is some evidence to show that the organism does not thrive in sewage or on bacterial beds, it seems desirable that a method of ensuring the absence of the organism in the sewage before reaching the sewage disposal works is to be desired, and the author submits the above as a method of solving this problem.

THE NOMENCLATURE OF THE IONS.*

By JAMES WALKER, F.R.S.

Anyone who has had to teach the theory of electrolytic dissociation must have found himself hampered by the want of a systematic and consistent nomenclature for the *material* of the the ions as distinguished from the particles themselves. Thus, whilst we may speak of hydrogen ions, chloride ions, or sulphate ions, meaning thereby the particles or molecules supposed to exist in aqueous solution, we have no systematic names for the substances which these supposed molecules constitute.

A basis for such a nomenclature was supplied by Faraday, who used the termination *ion* in conjunction with the stems of the ordinary chemical names. Thus, *sulphion* was the negative ion or radical of the sulphates, *nitrion* of the nitrates, and so on.

It is evident, however, that in the form used by Faraday these names are inadequate. Sulphion might be derived from sulphate, sulphite, or sulphide; there is nothing in the name to indicate which. On the Continent, and even in this country, the names *sulphation*, *sulphition*, and *sulphidion* have been proposed to overcome this difficulty. But it is obviously doing violence to the principles of English pronunciation (such as they are) to speak "sulphation" otherwise than as a rhyme to "relation," or "sulphition" otherwise than as a rhyme to "condition." The terminations *ation* and *ition* must be discarded unless we are to make our chemical terminology even more arbitrary and confusing than it is at present.

The proposals which I make for naming the positive and negative radicals of salts, acids, and bases considered as ions are as follows:—

For positive radicals or kations the name is obtained by adding the termination *ion* to the stem, and prefixing where necessary a Greek numeral to indicate the electrical charge or valency of the radical. Thus, if we use with Ostwald a dot to express unit positive charge, we have for some typical kations:—

Hydrion	$H^{\cdot}$	
Sodion	$Na^{\cdot}$	
Ammonion	$NH_4^{\cdot}$	
Potassion	$K^{\cdot}$	
Calcion	$Ca^{\cdot\cdot}$	
Barion	$Ba^{\cdot\cdot}$	
Monomercurion	$Hg^{\cdot}$	(in mercurous salts)
Dimercurion	$Hg^{\cdot\cdot}$	(in mercuric salts)
Diferrion	$Fe^{\cdot\cdot}$	(in ferrous salts)
Triferrion	$Fe^{\cdot\cdot\cdot}$	(in ferric salts)
Chromion	$Cr^{\cdot\cdot\cdot}$	

For negative radicals or anions the name is obtained by substituting, in accordance with the following table:—

Termination of salt radical.	Termination of anion.
—ate	—anion
—ite	—osion
—ide	—idion

These terminations for the anions are all compound, and easily distinguishable from the simple termination of the kations. The termination *anion* was selected because it begins with the same vowel as *ate*, and is for the rest self-explanatory. The termination *osion* was chosen because it indicates connection with the *ous* acids from which the *ites* are derived.

The following are some typical anions, each dash attached to the formula indicating unit negative charge:—

Hydroxidion	OH'
Sulphidion	S''
Sulphosion	SO_3''
Sulphanion	SO_4''
Chromanion	CrO_4''
Carbanion	CO_3''
Orthophosphanion	PO_4'''
Metaphosphanion	PO_3'
Chloridion	Cl'
Chloranion	ClO_3'
Hypochlorosion	ClO'
Acetanion	$C_2H_3O_2'$

Anions, such as H_2PO_4' and HPO_4'' (from NaH_2PO_4 and Na_2HPO_4), may be named *dihydrophosphanion* and *hydrophosphanion* respectively. The anion HCO_3' of the bicarbonates would be thus called *hydrocarbanion*.

The complex anion $Ag(CN)_2'$ from potassium-silver cyanide would, on the above system, receive the name *argenticyanidion*; the anion AgS_2O_3 *argentithiosulphanion*, and so on. If the system is consistently applied, there is no difficulty in finding names for the ions if we have a name for the salt from which they are derived.

The only instances in which the system might lead to any ambiguity are those complex kations, in which the Greek numerals are used in the ordinary chemical manner, and might possibly be confused with the prefixes indicating charges. But as these prefixes are required in the second sense practically for simple kations only, there is no real risk of ambiguity or confusion.

The system, although devised for English, might, with appropriate alterations, be easily adapted to other languages.

The use of the above compound names in the molecular as opposed to the substantial sense should be carefully avoided. Thus, *a chloridion* or *chloridions* (to indicate *chloride ions*) should never be used. We should no more speak of *a chloridion* or *chloridions* than of *a chlorine* or of *chlorines*. If we wish to indicate the particles we ought to say *chloride ions*, as formerly, or *chloridion molecules*.

It may seem to some that the matter here discussed is trivial, but it appears to me that if a system such as I have proposed had been adopted when the ionisation hypothesis was first brought forward a great deal of mis-

* Read before the British Association (Section B), Glasgow Meeting, 1901.

apprehension might have been avoided. To say that sodium chloride when dissolved in water is partially decomposed into the substances *sodium* and *chlorine* is altogether misleading; to say that it is partially decomposed into the substances *sodion* and *chloridion* is quite a different statement, and one with a clear and definite meaning. Sodium is no more sodion than oxygen is ozone, or graphite diamond.

University College, Dundee.

THE MINUTE STRUCTURE OF METALS.*

By G. T. BEILBY.

Microscopic examination of metallic surfaces produced by breaking, tearing, or filing, by rolling, drawing, hammering, or polishing, has shown that the metals, as they are ordinarily met with, appear in two forms:—

(*a*) As minute scales or "spicules."
(*b*) As a transparent glass-like substance.

These two forms of "metal substance" occur in all the metals examined, and, taken together, they do not appear to depend in any way on the particular thermal or mechanical treatment to which the metal has been subjected, nor upon the greater or less mass of the particular piece of metal examined. Their existence is, therefore, to a great extent, independent of the conditions which determine the particular crystalline structure in metals and alloys.

In form (*a*) the scales or "spicules" do not vary much in size in the different metals examined, which include among their number representatives of most of the great groups. The diameter of the scales is estimated to range from $\frac{1}{500}$ to $\frac{1}{100}$ of a millimetre. Their thickness has not yet been measured, but they can be seen by reflected light, when their thickness is certainly less than $\frac{1}{12000}$ of a millimetre.

Form (*b*) is seen as a transparent glass-like film on metal surfaces which have been exposed to certain forms of pressure. In the transparent form the metals have their characteristic colours by transmitted light; for instance, gold is green, iron is blue.

The scale form (*a*) passes into the transparent form (*b*) when the metal is pressed or hammered upon a hard polished surface. The same effect takes place when a mirror-like polish is produced by ordinary methods. Files or cutting tools, in passing over the surface or through the substance of metals, leave the cut or scraped surface covered with a more or less continuous film of transparent metal. All polished metallic surfaces are covered with a thin layer of transparent metal like a lacquer or enamel.

By suitable treatment, a coating of transparent metal can be formed of varying degrees of thickness, so that, by reflected light, scales can be seen more or less deeply embedded in the transparent coating. The light from the deeper scales shows the characteristic colour of the metal. In some cases the colour of the coating, as seen by the microscope, is so intense that no reflected light reaches the surface.

Attempts have been made to measure the thickness of the transparent film by focussing for its upper and lower surfaces, or for the upper surface, and for scales embedded in the film, and measuring the movement of the microscope between these points. As the measurements appear to give rather exaggerated results their publication is held over for the meantime.

The transparent metal (*b*) passes back into the scale form (*a*) under the influence of certain kinds of mechanical and chemical treatment.

The metals already examined include gold, silver, platinum, cobalt, nickel chromium, iron, copper, lead, bismuth, antimony, tin, cadmium, magnesium, aluminium, zinc, and sodium.

The highly crystalline metals, such as antimony, bismuth, and zinc, exhibit the same features as the softer and more malleable metals. The crystalline faces and cleavages are covered with a film of transparent metal, while scales are distinctly seen in fractures at right angles to the cleavage planes. Certain ores show similar appearances.

The zinc and tin alloys of copper show the same minute structure and appearances as the pure metals.

The persistence of these minute scales or "spicules" under all kinds of mechanical and thermal treatment, the remarkable uniformity of their size and appearance in metals of all the leading groups, their disappearance into the transparent form, and their re-appearance again, apparently unchanged in size or otherwise, seem to afford fair ground for the conjecture that they are, in some way, definite units in the structure of metals.

* Abstract of a Paper read before the British Association (Section B), Glasgow Meeting, 1901.

ALUMINIUM-TIN ALLOYS.*

By W. CARRICK ANDERSON, M.A., D.Sc.,
and
GEORGE LEAN, B.Sc.

This investigation was undertaken to ascertain, with some definiteness, the general properties of the alloys of aluminium and tin, and particularly the cause of the peculiarity, first pointed out by Riche (*Journ. Pharm. Chem.*, 1895, I., v.), that the alloy containing 25 per cent aluminium evolves hydrogen freely when placed in water. This property was found to belong, not only to the particular alloy in question, but to the whole series, whether cast or annealed.

From the determinations of the cooling curves it is shown that tin dissolves in aluminium, but that in the case of alloys containing more than 10 per cent tin a second break in the cooling curve takes place at 232° C., indicating an excess of tin (Gautier, *Comptes Rendus*, 1896, cxxiii., 109). Microphotography was also employed to show the structure of the alloys in the cast and annealed condition. The amounts of hydrogen evolved from the several alloys, cast and annealed, were found to stand in no simple relation either to the weights of the constituent metals present, or to the depression in the aluminium melting-point.

From microscopic examination of water-corroded plates the conclusion is arrived at that contact action between the tin and the stanniferous aluminium is mainly responsible for this spontaneous oxidation.

* Read before the British Association (Section B), Glasgow Meeting, 1901.

ON THE

POSSIBILITY OF SYSTEMATIC ERROR IN PHOTOGRAPHS OF A MOVING OBJECT.†

By ARTHUR R. HINKS.

As a preliminary to the discussion for a determination of the Solar Parallax of a series of photographs of the planet Eros, made last winter by the author at Cambridge Observatory, it was essential to assure one's self that no systematic error was produced by the motion of the planet during the exposure (generally three or two minutes). Two series of plates were taken—(*a*) with stars fixed and planet trailing; (*b*) with planet fixed and stars trailing.

It is easy to imagine how such an error might arise. Owing to atmospheric disturbance, the image of a star during exposure is buzzing about on the plate around its

† Read before the British Association (Section A), Glasgow Meeting, 1901.

mean position. The developable image is thereby enlarged, and a larger area still on the sensitive film is prepared for decomposition, just as very sensitive plates are prepared by preliminary exposure to faint light. Consequently, if the image is trailing on the plate, it is trailing on to a surface already prepared to the point of decomposition, and it seems possible that the centre of the developed image might therefore be in advance of its true place.

The author shows (1) that if such an effect were independent of the magnitude of the star, the two series (*a*) and (*b*) would be rigorously comparable with one another, but each would give the place of the planet with respect to the stars ahead of its true position by the same amount; (2) that it is almost certain, however, that the effect would depend on the brightness of the star; (3) that a comparison of the two series of plates gives no evidence of the existence of a differential effect varying with the magnitude of the star; and (4) that the absolute error is therefore probably also insignificant.

UTILISATION OF NASCENT CARBON DIOXIDE AS A CHEMICAL REAGENT.

By H. NICHOLSON.

In the manufacture of chemicals carbon dioxide plays a somewhat important part. Up to the present time conjunction in the form of an alkaline carbonate or bicarbonate has been the usual manner of conveyance, inasmuch, of course, that any acidity of suspending liquid prevents the formation of carbonates.

During some experiments on a fairly large scale with explosive mixtures of air and inflammable gases, burning them in a specially constructed burner under water, it occurred to me that the CO_2 (the product of the combustion)—formed, as it is, in direct contact with, and under the surface of, the water—might possess increased activity at the moment of its generation, and decompose some salts of metals having insoluble carbonates and in which it is in ordinary circumstances necessary to bring about decomposition with alkaline carbonates.

My first experiments have been on borate of calcium.

On suspending finely-ground borate of calcium in water, and boiling with the flame of air and gas (producer gas), immersed and in actual contact with the liquid, decomposition occurs. Under ordinary circumstances boracic acid decomposes calcium carbonate slowly, but in the presence of nascent CO_2 calcium carbonate is formed and boracic acid goes into solution.

On withdrawing the burner, and so removing the influence of nascent gas, the free acid commences to decompose the $CaCO_3$ and re-form calcium borate. The effect of the burner is an interesting example of the influence of nascent gases on chemical equilibrium, and opens up a large field for research.

The combustion of gases under water and in actual contact is unique, presenting a new sphere of possibilities in chemical reactions.

THE ESTIMATION OF CARBONIC ACID IN WATER.*

By JOSEPH W. ELLMS and JAY C. BENEKER.

(Concluded from p. 159).

Comparison of the Three Methods on Waters containing Known and Unknown Amounts of Carbonic Acid.

THE comparison of the results obtained with known solutions of carbonic acid indicate the relative and actual accuracy of these three methods. Solutions containing known amounts of free and half-bound carbonic acid were prepared by neutralising partially or wholly measured quantities of a 0·02 normal solution of sodium carbonate with a 0·02 normal solution of sulphuric acid. Solutions of calcium and magnesium salts were introduced in order that these bases might be present and thus produce an artificial water having approximately the same composition as natural waters.

The first table shows the amount of free carbonic acid obtained in a solution known to contain 44 parts per million. This solution contained no calcium or magnesium salts. The term "Trillich method" has been used in the column headings of the following tables in the sense in which it was defined in the first portion of this paper. Strictly speaking, in the absence of magnesium salts, where the use of ammonium chloride is unnecessary, the columns could have been headed "Pettenkofer method"; but, to avoid confusion, the definitions first given have been adhered to.

Table showing Free Carbonic Acid found in a Solution known to contain 44 Parts per Million.

No.	Trillich method. Parts per million.	Seyler method. Parts per million.
1	41·7	44·2
2	43·7	44·7
3	42·2	44·2
4	40·8	43·8
5	42·7	44·0
6	41·7	43·6
7	40·8	44·4
Average	42·0	44·0

When free and half-bound carbonic acid were present together in known amounts the following results were obtained:—

Table showing Free and Half-bound Carbonic Acid found in a Solution known to contain 8 Parts Free and 40 Parts Half-bound Carbonic Acid. (Free and Half-bound Acid equals 48 Parts Per Million).

No.	Trillich method. Free and half-bound acid. Parts per million.	Seyler method. Free acid. Parts per million.	Seyler method. Half-bound acid. Parts per million.	Seyler method. Free and half-bound acid. Parts per million.
1.	47·0	7·0	40·8	47·8
2.	46·1	6·2	41·3	47·5
3.	46·1	6·6	41·3	47·9
4.	47·0	7·0	41·3	48·3
5.	47·0	7·9	41·3	49·2
6.	45·0	7·9	41·3	49·2
7.	45·4	7·5	41·3	48·8
8.	46·1	7·9	40·8	48·7
9.	46·1	7·0	41·3	48·3
10.	46·1	7·9	41·3	49·2
Average	46·2	7·3	41·2	48·5

The following table shows the results obtained with these methods when the solution contained double the amount of free and half-bound carbonic acid as was present in the solution from which the figures in the preceding table were obtained:—

Table showing Free and Half-bound Carbonic Acid found in a Solution known to contain 16 Parts Free and 80 Parts Half-bound Carbonic Acid. (Free and Half-bound Acid equals 96 Parts per Million).

No.	Trillich method. Free and half-bound acid. Parts per million.	Seyler method. Free acid. Parts per million.	Seyler method. Half-bound acid. Parts per million.	Seyler method. Free and half-bound acid. Parts per million.
1.	92·2	15·8	78·2	94·0
2.	91·0	14·5	81·1	95·6
3.	91·0	14·1	81·1	95·2
4.	90·5	14·5	80·2	95·2
5.	90·5	15·0	80·2	94·7
Average	91·0	14·8	80·1	94·9

* *Journal of the American Chemical Society*, xxiii., No. 6.

No attempt has been made in our work with Pettenkofer's and Trillich's methods to differentiate by titration (according to Trillich's method) the free carbonic acid from the half-bound. Assuming, however, that the half-bound acid in the above solution is, as shown by the average, 80·1 parts per million, then the free carbonic acid by Pettenkofer's or Trillich's method would be 91 parts minus 80·1 parts, or 10·9 parts per million.

In the following table are shown comparisons made with solutions containing known amounts of free and half-bound carbonic acid, and which also contained varying but known amounts of magnesium salts.

Table showing Free and Half-bound Carbonic Acid found in Solutions known to contain 4·9 Parts Free and 41·6 Parts per Million of Half-bound Carbonic Acid, and with Varying Amounts of Magnesium Sulphate. (Free and Half-bound Acid equals 46·5 Parts per Million).

No.	Magnesium sulphate present equivalent to carbonic acid.	Pettenkofer method. Free and half-bound carbonic acid.	Trillich method. Free and half-bound carbonic acid.	Seyler method. Free carbonic acid.	Half-bound carbonic acid.	Free and half-bound carbonic acid.
	Parts per million.	Parts per million.	Parts per million.	Parts per million.	Parts per million.	Parts per million.
1.	10	44·6	43·9	4·6	48·2	45·8
2.	10	43·1	43·9	—	—	—
3.	10	43·1	44·4	—	—	—
4.	20	41·5	45·6	4·3	41·2	45 5
5.	20	44·6	44·2	4·0	41·9	45·9
6.	40	44·6	43·3	4 0	42·6	46·6
7.	40	43·1	40·4	4·6	41·2	45·8
8.	40	46·0	40·4	—	—	—
Average ..		43·8	43·2	4·3	41·6	45·9

Assuming, as in the preceding tables, that the half-bound carbonic acid is on an average 41·6 parts per million in the above solution, then the Pettenkofer results indicate 2·2 parts per million of free carbonic acid and the Trillich results 1·6 parts per million.

Comparisons were also made on natural waters containing unknown amounts of free and half-bound carbonic acid. The first table given below shows the results obtained on a sample of Ohio river water by the three different methods. This sample of water contained, by a gravimetric determination, 10 parts per million of magnesium oxide, equivalent to a correction to be applied to the Trillich figures of 11 parts per million.

Table showing Amount of Carbonic Acid found in Ohio River Water by the Three Methods.

No.	Pettenkofer method. Free and half-bound carbonic acid.	Trillich method. Free and half-bound carbonic acid.	Seyler method. Free carbonic acid.	Half-bound carbonic acid.	Free and half-bound carbonic acid.
	Parts per million.	Parts per million.	Parts per million.	Parts per million.	Parts per million.
1.	14·9	15·4	0 6	16·2	16·8
2.	14·9	16·8	0·4	16·4	16·8
3.	13·4	16·1	0·4	16·2	16·6
4.	14·4	16·8	0·4	16·6	17·0
5.	14·4	16·8	0·6	16 6	17·2
6.	14·4	16·1	0·6	16·2	16·8
7.	13·4	16·8	0·4	16·4	16·8
8.	14·9	15·4	0·4	16·6	17·0
9.	13·2	16·8	0·4	16·6	17·0
Average	14·2	16·3	0·4	16·4	16·8

The following well-water was also examined, and is given as an illustration of a water highly charged with carbonic acid and containing a large quantity of mineral salts, especially those of magnesium. A gravimetric determination of the calcium and magnesium, and also of the sulphuric acid, gave the following results:—

Well-water.

	Parts per million.
Lime (CaO)	378
Magnesia (MgO)	128
Sulphuric acid (SO_3)	351

The free and half-bound carbonic acid were determined by the three volumetric methods, and the results obtained are shown in the following table:—

Table showing Amount of Carbonic Acid found in a Well-water by the Three Methods.

No.	Pettenkofer method. Free and half-bound carbonic acid.	Trillich method. Free and half-bound carbonic acid.	Seyler method. Free carbonic acid.	Half-bound carbonic acid.	Free and half-bound carbonic acid.
	Parts per million.	Parts per million.	Parts per million.	Parts per million.	Parts per million.
1.	241	242·4	63·4	176·4	239·8
2.	241	236·5	66·9	176·4	243·3
3.	241	236·5	68·6	176·4	245·0
4.	241	246·3	65·1	177·4	242·5
5.	238	242·4	68·6	176·4	245·0
Average	240·4	240·8	66·5	176·6	243·1

As would be expected, the variation in the above results is in some cases considerable, but the greatest difference is less than 10 parts per million, and the greatest variation from the mean of all the results is less than 5 parts per million.

The results of the above analyses were all obtained on waters which when cold reacted neutral or acid to phenolphthalein. There is one other class of waters which when cold react alkaline to phenolphthalein, and which, in consequence, require a modification of Seyler's method, as previously described. The number of waters belonging to this class does not seem to be at all large, and the writers have never examined but one water which showed this feature. Seyler states that pure sea-water is alkaline to phenolphthalein. He gives the following analysis:—

	Parts per million.
Free carbonic acid	0
Half-bound carbonic acid . ..	44·0
Fixed carbonic acid	51·7
Total carbonic acid ..	95·7

He also states that he has found well-waters which, upon standing exposed to the air for some time, reacted alkaline to phenolphthalein, and that such waters contained considerable magnesium carbonate.

The writers have found that, at certain times, the Mississippi river water is alkaline to phenolphthalein. How long such periods last or at what seasons of the year they occur we have not had the opportunity to determine. It is quite probable that the so-called "alkali waters" of the Western plains would react alkaline to phenolphthalein, as they contain carbonates of sodium. It has been noted that water which has stood in the iron pipes of the laboratory for some time, will, when first drawn, react alkaline to phenolphthalein. This is due probably to the free carbonic acid and bicarbonates in the water reacting with the iron of the pipe to form carbonate of iron, and thus leaving in solution small amounts of normal calcium and magnesium carbonates.

The water examined by us which reacted alkaline to phenolphthalein was a mixed sample of Mississippi river water. The samples were taken during the month of September, 1900, opposite Quincy, Illinois. When examined it was found to give a strong pink colour with phenolphthalein. Its average approximate composition was as follows:—

	Parts per million.	
Lime (CaO)	35·6	equivalent to 63·5 parts $CaCO_3$.
Magnesia (MgO)	16·0	equivalent to 33·6 parts $MgCO_3$.
Sulphuric acid (SO_3) ..	7·2	
Chlorine (Cl)	6·3	
Fixed carbonic acid (CO_2)	39·8	equivalent to 90·4 parts when expressed in the form of calcium carbonate.

From a consideration of these results, it is more than probable that the magnesium was present partly as normal magnesium carbonate ($MgCO_3$), and the calcium as calcium bicarbonate. Only a limited quantity of the sample was available for experimental purposes. The following table shows the average of the results obtained in determining the carbonic acid by the three volumetric methods:—

Carbonic Acid obtained in a Sample of Mississippi River Water.

	Parts per million.
Pettenkofer method—	
Free carbonic acid	0
Half-bound carbonic acid	0
Trillich method—	
Free carbonic acid	0
Half-bound carbonic acid	34·6
Seyler method—	
Free carbonic acid	0
Half-bound carbonic acid	35·4

Seven different portions of this water treated according to Pettenkofer's method showed that in no instance was any barium hydroxide used up, and that, on an average, only 60 parts per million (expressed in terms of $CaCO_3$) of carbonates were precipitated out, which still left in solution about 30 parts per million. The reason for this is not clear, but it is probable that the ammonium chloride used was one factor which was instrumental in holding a portion of the carbonates in solution. Whether the dissolved organic matter, which was in considerable amount, was another cause of such unusual results, we are unable to state.

An artificial water prepared so as to contain approximately the same amounts of calcium and magnesium carbonates as were present in the Mississippi river sample, gave the following results:—

	Parts per million.		
	No. 1.	No. 2.	Average.
Pettenkofer method—			
Free carbonic acid	0	0	0
Half-bound carbonic acid	27·9	29·4	28·7
Trillich method—			
Free carbonic acid	0	0	0
Half-bound carbonic acid	31·6	31·6	31·6
Seyler method—			
Free carbonic acid	0	0	0
Half-bound carbonic acid	31·7	32·2	31·9

This water contained 11 parts per million of magnesium oxide, equivalent to a correction in the Trillich method of 12 parts per million.

The tendency here is for Pettenkofer's method to give low results, but the carbonates are not affected to the extent that they were in the river water.

Conclusions.

From a consideration of the data obtained in this investigation, it appears that the Lunge-Trillich or Seyler method is the most accurate of the three volumetric methods. The "free and half-bound carbonic acid," as determined on known amounts by this method, is, on an average, less than 1 per cent too low, and shows a possible range of less than ± 3 per cent. The accuracy of the determination of the "free carbonic acid" is somewhat less, and although the percentage error for low amounts is rather high, the variation from the actual amount is not more than 2 to 3 parts per million. These results are always too low, and introduce into the determination of the "volatile carbonic acid" the larger proportion of the error.

Trillich's modification of Pettenkofer's method is less accurate than the Seyler method, but more accurate than the Pettenkofer. Results obtained with either Pettenkofer's or Trillich's method are almost always too low. They probably give figures which are, on an average, between 5 and 10 per cent too low. While Trillich's method gives more uniform results than Pettenkofer's, the figures appear to be about 5 per cent too low, and they may be as much as 10 or 12 per cent too low.

Pettenkofer's method is inclined to give still lower results, and although those obtained seemed to be only from 1 to 2 per cent lower than those obtained with Trillich's method, yet it appears somewhat unreliable, and one in which, under some conditions, extremely erratic results are likely to occur. With very low amounts of carbonic acid the percentage error in both Pettenkofer's and Trillich's methods are much greater than those stated above, although it may only represent an actual difference of from 3 to 4 parts per million.

For ease and rapidity of manipulation, for avoidance of difficulties arising from the presence of magnesium salts, and for its greater accuracy, the Lunge Trillich or Seyler method is, in the opinion of the writers, to be preferred to either of the other two volumetric methods.

CONTRIBUTIONS TO THE SCIENCE OF THE NITROCELLULOSES.*

By G. LUNGE and J. BEBIE.

(Continued from p. 153).

In order to determine whether the presence of nitrous acid in the nitration mixtures tends to diminish the stability we proceeded as follows:—

Two nitrations were carried out with the same nitration mixture; one containing a certain quantity of nitrous acid, and the other without any. The two nitrations were started simultaneously, and the two products of nitration to be compared received exactly similar treatment as regards washing, drying, and application of the stability test. The great sensitiveness of the latter, and the numerous factors which influence it, have made this method of work necessary. The attempt was first made to carry out only one nitration with the nitration mixture free from nitrous acid. The resulting gun-cotton was treated according to the prescribed manner, and the stability then determined. We hoped to obtain comparable results from products arising from exactly similar treatment and containing various amounts of nitrous acid. But this did not prove to be the case; the results thus obtained were often quite contradictory. Hence, these experiments are here passed over, and we pass on to those conducted at the same time, according to the method above mentioned.

Experiment 1.—Two nitrations were undertaken at the same time and under exactly similar conditions, and with the mixture usual in trade of three parts concentrated sulphuric acid and one part nitric acid 1·52; one operation without addition of nitrous acid, the other with addition of 4·93 per cent N_2O_4, determined by titration with N/2 potassium permanganate. In the latter case, according to the reaction $N_2O_4 + H_2SO_4 = SO_2NH + HNO_3$, a certain amount of nitric acid is introduced into the nitration mixture through the nitrous acid present. An exactly equal quantity of pure nitric acid was therefore

* *Zeitschrift fur Angewandte Chemie*, 1901, Heft 20.

Abel Test.

Day of the experiment.	Without nitrous acid.		With nitrous acid.		Check experiment
	a_1.	a_2.	b_1.	b_2.	c.
5/12/1899	25′ E.P. = 188·5° t = 5′ 11″	27′	37′ E.P. = 188° t = 5′ 10″	36′	14′ E.P. = 195° t = 6′
12/1/1900	44′	45′ E.P. = 187° t = 5′ 35″	52′	50′ E.P. = 186° t = 5′ 33″	13′ E.P. = 201° t = 4′ 30″
6/3/1900	55′ E.P. = 187° t = 5′ 30″	54′	64′ E.P. = 186·5° t = 5′ 29″	64′	15′ E.P. = 196° t = 6′

The first numbers indicate the time that elapses before the reaction sets in.
E.P. = explosion-point.
t = time of heating till explosion occurs.
Temperature of water-bath = 80°.

added to the mixture containing no N_2O_4, in order to establish similar conditions, as far as possible, in both experiments. The nitration products were then submitted to exactly similar treatment, and, after pressing out the acids and repeated washing with cold water, were cut up as finely as possible with scissors, boiled for four days in large porcelain dishes with frequent renewal of the water, then well pressed between blotting-paper, and finally placed in a vacuum desiccator for about six days until completely dry. The substances must be as dry as possible for carrying out the stability test, as the presence of a very small amount of moisture may considerably retard the beginning of the reaction. In order to check the unchanged sensitiveness of the test-paper, a sample of known stability was tested with each determination. The material used for this purpose was kept in a moist condition in a closed flask.

Together with the stability test, the explosion temperature of the product was generally determined by heating 0·01 grm. in a little glass placed in an oil-bath. The explosion temperature is dependent on the duration of the heating, to which it is inversely proportional.

At the termination of the stability test, the products were spread out on lunette glasses and allowed to lie exposed to the air, but protected from dust. From time to time their stability was again tested; once to determine the effect of long standing, and afterwards to confirm the results with a large number of determinations.

Two samples of each product, of 1·2 grms. each, were always tested simultaneously. All the determinations were carried out together and in the same apparatus.

Thomas's test.	Number of days.
a_1	2½
b_1	3
c	2

In this experiment, therefore, a diminution of stability owing to the presence of nitrous acid in nitrating cannot be proved. The gun-cotton produced by nitrating in the presence of nitrous acid even showed more favourable stability results, which must certainly not be attributed to the action of the nitrous acid, but must be mentioned as a fact. The explosion of this product occurred one to two seconds earlier, and the temperature was ½—1° lower than in the case of the gun-cotton produced from the nitration mixture containing no nitrous acid. But this difference is so slight that no real importance attaches to it. The explosion-points of the one product, a and b, were determined simultaneously in the same oil-bath; hence, the manner and speed of heating was the same for both, and accordingly the results may be directly compared with one another. The two explosions always followed each other quickly, often with a scarcely measurable time difference. It is remarkable that the explosion-point of c lies about 10° higher than that of products a and b. It follows that the beginning of the decomposition (stability test) and the setting in of a sudden and complete decomposition (explosion-point) do not stand in a simple relation to one another.

(To be continued).

THE ANALYSIS OF WHITE-METAL ALLOYS.

By FRED. IBBOTSON and HARRY BREARLEY.

Introduction.

It has been said again and again, and it is unquestionably true, that the analyst is better equipped with processes for the analysis of iron and iron alloys than he is with means of examining any other complex metallurgical compounds. This is particularly true in relation to the analysis of alloys of white-metal, such as are used for anti-friction purposes and better class type-metals.

Close attention to and some experience with nearly every scheme which has been proposed for analysing anti-friction metals leads us to conclude that:—

(1). While there are many processes which yield amounts of tin, antimony, lead, copper, bismuth, arsenic, &c., that total up to about 100 per cent, there are very few which give satisfactory results for the individual metals when applied to known amounts of them dissolved up altogether; and

(2). That some means of estimating the elements singly without any preliminary separations, or merely incidental ones, as is so common in the everyday analysis of iron compounds, would be a great advantage when only partial analysis were needed, and would also be most desirable checks on the results of a general analysis.

In the following series of papers we propose, as opportunity is afforded us, to show how an estimation of a number of specific elements may be made singly; and then to describe a process for the general analysis of white-metal alloys which has yielded excellent results with mixtures of known composition in a comparatively short time.

I. *The Estimation of Tin.*

The titration of a hydrochloric acid solution of stannous chloride with iodine has been several times recommended as an easy and accurate means of estimating tin. The reduction of stannic to stannous chloride is generally accomplished by metallic iron, since ferrous salts do not at all interfere with the subsequent titration; this makes the process a particularly desirable one for the assay of tinned-plate.

Whether the measured oxidation of stannous to stannic salts is made in acid or alkaline solution, the avidity with which the former, particularly when hot, absorb oxygen

from the air or from water used for dilution must be guarded against. Any error is reduced to a minimum by cooling the reduced solution in an atmosphere of CO_2, and adding nothing to it save the standard iodine and starch.

A very brief exposure of hot solutions of stannous chloride to the atmosphere is undesirable, and therefore the iron which is added in excess of that needed for the reduction of the tin must be completely dissolved. When antimony is also present, it is reduced by the iron to the metallic state, and as it is quite insoluble in hydrochloric acid no amount of boiling enables these metallic flocks to be got rid of. If the solution be carefully cooled in an inert atmosphere, and the antimony be filtered off, it is necessary only to again reduce the filtrate with iron and titrate the tin, but if the hot solution be filtered a portion of the antimony goes into solution and is again precipitated by the iron.

The antimony found in the filtrate when hot solutions of stannous chloride containing that metal are filtered, is due to the formation of stannic chloride by the oxygen of the atmosphere, and a further reduction of the same by metallic antimony. When filtered cold, not nearly so much stannic chloride can be formed, and, moreover, *cold acid solutions of stannic chloride are not reduced by metallic antimony.*

From the above, it follows that a solution containing tin and antimony may be reduced with iron, cooled in an inert atmosphere, and titrated with iodine without troubling at all about the precipitated Sb. So little is the precipitated antimony affected by the cold stannic chloride that, after the titration of the tin, it may be filtered off and estimated with very tolerable results in any of the usual ways. The following analyses are presented in support of these conclusions :—

Grm. taken.		Grm. found.	
Tin.	Antimony.	Tin.	Antimony.
0·2000	0·0400	0·2000	—
0·1200	0·1000	0·1204	0·0972
0·1000	0·1200	0.1003	0·1152
0·0400	0·2000	0·0401	—

The accurate estimation of tin in the presence of antimony is the point we are insisting upon ; the simultaneous estimation of antimony is but incidental, and must in practice always give results somewhat low, particularly when the tin is very large in comparison with the antimony.

Antimony which has been precipitated with iron from its chloride solution does *very slowly* reduce stannic chloride in cold solutions, and therefore the starch blue in the above series of titrations is not quite permanent. But smelted antimony which has been ground in an agate mortar has a scarcely preceptible reducing action on cold stannic chloride, although at boiling-point it very quickly reduces it to stannous chloride. To a hydrochloric acid solution of stannic chloride there was added a few decigrms. of powdered antimony. The solution was boiled, cooled in CO_2, and titrated with iodine. One-tenth of a c.c. of N/10 iodine was added in excess in order to form a very decided blue colour. After standing for fifteen minutes the colour had not gone. It did not disappear on heating until 60° C. was reached; and, at that temperature, it disappears very lazily on reforming with a drop of iodine.

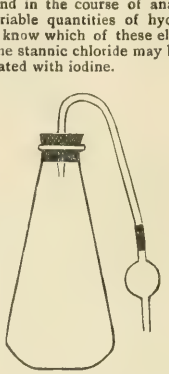
The following test analyses show that the tin is completely reduced to stannous chloride by the antimony :—

Tin added.	C.c. N/10 I used.	Tin found.
0·1750	29·7	0·1752
0·1000	16·9	0·0997
0·0480	8·3	0·0490
0·0200	3·4	0·0201
0·0080	1·4	0·0083

The reduction of stannic chloride with antimony instead of with iron or zinc, or any other metal, is obviously an improvement in so far as any excess added need neither be destroyed in the solution nor otherwise removed. In a measure, too, the excess of antimony acts as a safeguard during the cooling of the $SnCl_2$, in that any accidental oxidation while the solution is still hot is corrected. As the solution cools, the antimony becomes less able to correct such a mishap ; which then, however, is less likely to occur.

The Estimation of Tin in the presence of other Elements.

In minerals and alloys tin is found associated with Fe, Mn, Al, Cr, Pb, Sb, Bi, Zn, Ni, Co, Hg, Si, Ag, Cu, S, P, As, W, and Mo, and in the course of analysis there accumulate very variable quantities of hydrochloric acid. It is desirable to know which of these elements *must* be separated before the stannic chloride may be reduced with antimony and titrated with iodine.



In each test 0·15 grm. of tin was used. The reduction was made in the arrangement shown in the figure, and cooled out of contact with air by dipping the tip of the bent tube into an emulsion of $NaHCO_3$ with freshly boiled water. By nipping the rubber connection at the right moment very little of the emulsion is needed to generate the required amount of CO_2, and it is desirable to use as little as possible in order to minimise the addition of dissolved oxygen.

Hydrochloric Acid.—Experiments in which the proportion of HCl (1·16 specific gravity), varied from one-tenth to one-half the volume (150 c.c.) of solution gave results varying from 99·5 to 101 per cent. It is desirable to work with solutions containing the same proportion of HCl, say one-fifth the volume of strong acid.

Iron.—Exercises no influence. When metallic iron is used to reduce the tin, and $SbCl_5$ is also present in solution, the appearance of metallic antimony is an indication that the tin is completely reduced. Much less iron may be used than is usual, and with greater certainty, by taking advantage of this fact.

Chromium and Nickel.—Exert no interference other than may be due to the colour of their chloride solutions, and that is not serious.

Zinc, Manganese, and Aluminium.—Do not at all interfere.

Copper.—Is reduced to cuprous chloride. If the iodine is added in brisk drops to the vigorously agitated solution, so that no local excesses of iodine are formed, the results are accurate. But the results are seriously out when local excesses of iodine are allowed; *e.g.*, only 0·1239 grm. tin was registered instead of 0·1500 when 20 c.c. N/10 iodine was run into the solution containing 0·05 grm. copper, without shaking, and then finished as usual. A white precipitate (cuprous iodide) forms. In order to delay the formation of this precipitate, and also to assist the precaution just named, it is advisable to have a larger proportion of HCl present ; say, one-third the volume of acid of 1·16 specific gravity.

Cobalt.—The results were always a trifle high, but it is

so little that one hesitates to say that cobalt exerts any influence; *e.g.*, 0·1510 grm. Sn instead of 0·1500.

Lead.—Without influence. In very dilute acid solutions lead iodide may form; but, by titrating in very acid solutions so as to prevent this, there is no difficulty when three or four times as much lead as tin is present.

Bismuth.—The yellow colour which bismuth forms in potassium iodide solutions does not interfere much with the starch blue. There is no other interference.

Arsenic.—Seriously interferes whether present as As_2O_3 or As_2O_5. A solution containing a decigrm. of arsenic and 0·15 grm. tin, treated in the usual way, needed only a few drops N/10 iodine to form the starch-blue. The same thing happens when the tin is reduced with iron. When acid solutions of soda arsenite and stannous chloride are boiled together a black graphitic-looking precipitate, insoluble in HCl, is formed. This precipitate, which contains both arsenic and tin, explains the interference.*

Phosphorus and Sulphur.—Soda phosphate and sulphate added to the stannic chloride exert no influence.

Mercury.—Is reduced to the metallic state. In hot solutions finely-divided mercury exerts a limited reducing action on stannic chloride; it is inert in cold solutions.

Molybdenum.—The characteristic Mo_2O_3 colour forms when the solution is but moderately warm, but it is not appreciably re-oxidised by the iodine. The starch-blue is very slowly discharged; this, however, leaves no uncertainty in the mind, because the normal end-reaction is so very sharp and decisive.

Tungsten.—Lower oxides are also formed. The solution may be light blue, but the starch (dark) blue can be readily distinguished notwithstanding.

The speed at which the reduction of the tin takes place depends very much on the state of division of the antimony. We use the metal ground in an agate mortar until the particles no longer glisten. With such material the reduction is completed by one minute's boiling.

It may sometimes be desired to repeat the estimation of the tin in the same liquid by again boiling, cooling, and re-titrating. This, however, cannot be done satisfactorily with metallic antimony as reducing agent. With iron, adding a few drops of $SbCl_5$ to show when all the tin is reduced, one and the same solution may be reduced and titrated as often as one pleases.

The Technical Department,
University College, Sheffield.

ON THE

PURIFICATION OF CÆSIUM MATERIAL.†

By H. L WELLS.

Several years ago (*Amer. Journ Sci.*, [3], xlvi., 186), I recommended the use of the yellow salt $2CsCl.PbCl_4$ as a means of precipitating cæsium from its solutions. Subsequent experience has shown that the method is very convenient for removing small quantities of the rare metal from all sorts of solutions; particularly from those from which the greater part of it has been precipitated by other means. For large quantities of cæsium, however, the lead tetrachloride method, used alone, is inconvenient on account of the large amount of chloride that must be used, and because it is possible to obtain only very dilute solutions of lead chloride or of the white double salt, $CsCl.2PbCl_2$ (*Amer. Journ. Sci.*, [3], xlv., 121).

I have used extensively the salt just mentioned as a means of precipitating cæsium from concentrated solutions of the crude extract of pollucite, made by means of hydrochloric acid. The precipitation is made by adding a hot concentrated solution of the calculated amount of lead nitrate. The precipitate is crystalline, and can be readily washed with dilute hydrochloric acid; then it can be very easily decomposed by boiling with ammonium carbonate solution. The method is satisfactory in a case where very little potassium and practically no rubidium are present, for, although it does not give a good separation from these metals, the precipitation of cæsium is nearly complete. The precipitate $CsCl.2PbCl_2$, however, is very heavy compared with the amount of cæsium that it contains, and its decomposition with ammonium carbonate produces four molecules of ammonium chloride for one of cæsium chloride. For these reasons the method has been abandoned in this laboratory in favour of the method of Godeffroy.

In precipitating cæsium according to Godeffroy's method I am accustomed to use less concentrated hydrochloric acid solutions than those that have been recommended. About one-third or one-half of the total volume of concentrated hydrochloric acid answers very well, and a solution of this kind possesses the advantage that it can be filtered by means of paper. To such a solution antimony trichloride, also dissolved in hydrochloric acid, is added as long as a precipitate forms. The latter is collected, best on a Büchner filter, and well washed with cold dilute hydrochloric acid.

To the filtrate and washings from the antimony salt, without concentrating them, lead nitrate is added at the rate of 2 or 3 grms. per litre. This salt should be dissolved in water before it is added. Chlorine gas is then passed in until the solution is saturated with it. After standing for a few hours the liquid is decanted from the precipitate of the salt Cs_2PbCl_6 (which is usually coloured green from the presence in it of the dark blue salt Cs_2SbCl_6),* and is tested by the addition of a little more lead nitrate, and chlorine also if necessary. This precipitation is so complete, as far as cæsium is concerned, that the liquid may be finally discarded. A litre of such a liquid will probably hold in solution only about 0·1 grm. of the salt Cs_2PbCl_6, but the rubidium salt is nearly one hundred times more soluble. The lead tetrachloride salt should be washed on a Büchner funnel with cold dilute hydrochloric acid.

Formerly I was accustomed to decompose the antimony salt, $3CsCl.2SbCl_3$,† by suspending it in water, and passing in hydrogen sulphide gas; but for large quantities this is a very slow and laborious operation, and it is much more convenient to treat it in a large porcelain dish with boiling dilute ammonium hydroxide. The antimonious oxide thus produced is dense and easy to filter and wash; moreover, it may be readily dissolved in hydrochloric acid, and used again for precipitating cæsium. A little antimony goes into solution in the ammonia, but this is readily removed, best after the liquid has become slightly acid by evaporation, by passing in hydrogen sulphide, and filtering.

The removal of ammonium chloride on a large scale by ignition is a very slow operation. It is therefore best, in most cases, after the hydrogen sulphide has been removed by evaporation, to add to the concentrated solution of cæsium and ammonium chlorides, in a large porcelain dish, a liberal amount of concentrated nitric acid, and to heat cautiously until frothing has ceased. When further additions of strong nitric acid produce no change of colour nor evolution of gas upon heating, the ammonium salts are entirely destroyed, and the cæsium chloride changed to nitrate.‡ The solution of cæsium nitrate in nitric acid is then evaporated to dryness, and the residue is heated until the acid nitrate§ is decomposed, and the normal

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* Some means of eliminating the arsenic will be noticed when the general analysis of the alloys is being dealt with

† Contribution from the Sheffield Laboratory of Yale University. From the *American Chemical Journal*, xxvi., No 3.

* Concerning this compound see *American Chemical Journal*, vol. xxvi., p. 268.

† The composition of this compound was very incorrectly determined by Godeffroy, who gave it the formula $7CsCl.5SbCl_3$. Setterberg first arrived at the correct formula, which was afterwards confirmed by Remsen and Saunders, and also by Muthmann, and by Wells and Foote.

‡ This method of destroying ammonium chloride is due to J. Lawrence Smith. See *Amer. Journ. Sci.*, [3], xxiv., 1.

§ A description of the acid cæsium nitrate will be published from this laboratory.

nitrate is more or less completely fused. The evaporation of the nitrate to dryness in the presence of nitric acid over a free flame in a dish is not a difficult operation, since decrepitation takes place to a much less extent than is the case when the chloride is evaporated in the same way. A large mass of fused cæsium nitrate should not be allowed to solidify quietly in the bottom of a porcelain dish, for on cooling it is liable to break the dish by its contraction. If it is stirred as it solidifies this danger is avoided.

Cæsium nitrate is one of the most beautiful of salts for re-crystallisation. Like potassium nitrate, it is much more soluble in hot water than in cold, and it crystallises upon slowly cooling a hot concentrated solution in the form of large, colourless prisms. I have found that re-crystallising this salt tends to purify it from traces of rubidium, for a large quantity of the salt which showed no rubidium spectrum, upon systematic re-crystallisation, showed a distinct spectrum for that metal in the final mother-liquor. This, however, is a slow method of purification if it is desired to carry the latter to the last degree, but the nitrate obtained by one or two re-crystallisations is pure enough for any ordinary purpose, unless the original antimony salt was contaminated to an unusual extent.

The nitrate is readily converted into carbonate by mixing it with two parts of pure oxalic acid, adding a little water, evaporating to dryness, and fusing the residue in a platinum crucible. (Method of J. Lawrence Smith, *loc. cit.*).

Where the highest degree of purity in a cæsium salt is desired, the salt $CsCl_2I$ (*Amer. Journ. Sci.*, [3], xlvi., 17), by its re-crystallisation, probably offers one of the best means for accomplishing that object. It is very much less soluble than the corresponding rubidium, potassium, sodium, and lithium salts. I have found that this salt may be made very conveniently from the nitrate by dissolving one part of the latter together with one atomic proportion of iodine in about ten parts of 1 : 1 hydrochloric acid at a temperature just below boiling. The solution takes place quickly, and, upon cooling, the beautiful yellow salt crystallises out. It is re-crystallised by solution in hot 1 : 1 hydrochloric acid and cooling. One or two re-crystallisations, when each crop is well drained and washed with a little cold dilute hydrochloric acid, give, even from impure materials, a remarkably fine product. From this trihalide by ignition, best at a very gentle heat so that the mass does not fuse, pure cæsium chloride may be prepared.

NOTES ON

LEAD AND CADMIUM FERROCYANIDES.*

By EDMUND H. MILLER and HENRY FISHER.

Lead Ferrocyanide.

THE following series of experiments were made in order to ascertain whether the composition of lead ferrocyanide is invariably $Pb_2Fe(CN)_6$, or whether, like the ferrocyanides of manganese and zinc, it is affected by the conditions of precipitation.

The precipitates were made as follows:—Lead acetate was dissolved in water and heated to boiling; to this a hot aqueous solution of potassium ferrocyanide was added, and acid in some cases, as is noted later. The precipitates were allowed to settle and were washed by decantation until free from lead or ferrocyanide, as indicated by hydrogen sulphide or by ferric chloride. They were then dried at 105° C. to constant weight. The method of analysis was in all cases as follows:—About 1 grm. was dissolved in dilute nitric acid in a casserole, and after the addition of sulphuric acid, evaporated to fumes. One evaporation was found to effect complete decomposition. The residue was taken up with 1 per cent sulphuric acid, to which half its volume of alcohol was added. The lead sulphate was washed with 1 per cent sulphuric acid containing alcohol, filtered, and weighed in a Gooch crucible. The iron was precipitated in the filtrate by ammonia, after boiling out the alcohol and adding ammonium chloride, filtered, washed, and weighed as Fe_2O_3. The filtrate from the iron was evaporated to dryness in platinum, the ammonia salts volatilised, and the potassium sulphate weighed.

A. Precipitate formed in a neutral solution with lead in excess settles rapidly. The analytical results are:—

	I.	II.	III.	Average.
Lead	66·03	66·15	66·09	66·09
$Fe(CN)_6$ ..	34·07	33·98	33·85	33·97
Potassium..	0·50	0·48	0·45	0·47
				100·53

B. Solution neutral, ferrocyanide in excess, the precipitate settles slowly. It gave on analysis:—

	I.	II.	III.	Average.
Lead	66·26	66·06	65·98	66·10
$Fe(CN)_6$ ..	33·54	33·77	33·90	33·70
Potassium..	0·62	0·55	0·58	0·58
				100·38

C. Solution slightly acid with acetic acid, lead in excess. The precipitate settles rapidly. On analysis, the following results were obtained:—

	I.	II.	III.	Average.
Lead	64·42	64·55	64·62	64·53
$Fe(CN)_6$ ..	35·48	35·33	35·37	35·39
Potassium..	0·84	0·81	0·80	0·82
				100·74

D. Solution slightly acid with acetic acid, ferrocyanide in excess. Precipitate settles rapidly. The results on analysis were almost identical with those obtained from the preceding precipitate.

	I.	II.	III.	IV.	Average.
Lead ..	64·43	64·28	64·38	64·58	64·42
$Fe(CN)_6$.	35·47	35·62	35·69	35·60	35·59
Potassium	0·82	0·76	0·86	0·79	0·81
					100·82

E. Solution strongly acid with acetic acid, ferrocyanide in excess. Precipitate settles badly. The results are:—

	I.	II.	Average.
Lead	63·73	64·02	63·87
$Fe(CN)_6$	35·51	35·02	35·26
Potassium	0·76	0·96	0·86

These and the following are results calculated from the determination of potassium, lead, and iron in undried portions, and consequently, when calculated from the ratio of Fe : K : Pb, add up to 100 per cent.

F. Solution strongly acid with hydrochloric acid, ferrocyanide in excess; precipitated hot as usual.

	I.	II.	Average.
Lead	63·02	63·39	63·21
$Fe(CN)_6$	34·74	34·48	34·61
Potassium	2·24	2·12	2·18

When the analysis is made on a sample dried to constant weight, it invariably adds up to a little over 100 per cent. This is probably caused by the fact that, on drying, the precipitates become either bluish or greenish in colour, due to a slight decomposition, so that the percentages of $Fe(CN)_6$, which are calculated from the iron, are high (for the CN : Fe ratio is higher in $Fe(CN)_6$ than in $Fe_7(CN)_{18}$ or $Fe_5(CN)_{12}$).

* Contribution from the Havemeyer Laboratories of Columbia University. From the *Journal of the American Chemical Society*, xxii., No. 9.

It is evident from these results that the precipitate varies in composition under different conditions of precipitation, and as the acidity increases the percentage of potassium increases and that of lead diminishes.

Also, that when the acidity is the same, the composition is the same whether ferrocyanide or lead is in excess.

Berzelius (*Ann. Chem. Phys.*, 1820, xv., 157) states that, when formed in a neutral solution with potassium ferrocyanide in excess, the composition of the precipitate is $Pb_2Fe(CN)_6$. Using the most recent atomic weights, this corresponds to a percentage composition of—

Lead	66·10
$Fe(CN)_6$	33·90

Our results are, with lead in excess :—

Lead	66·09
$Fe(CN)_6$	33·97

With ferrocyanide in excess :—

Lead	66·10
$Fe(CN)_6$	33·70

The only statement we have found suggesting any variation in the composition of this ferrocyanide is by Gay-Lussac ("Gmelin's Handbook of Chemistry," London, 1852, vol. vii., p. 490) that "the precipitate, for however long a time it may have been washed, retains from 6 to 9 per cent of ferrocyanide of potassium; of which it continues to give up a certain quantity to fresh portions of water." The conditions of this precipitation are not stated.

In order to compare these results with those obtained by titration, the following experiments were made :—A solution of potassium ferrocyanide was very carefully standardised against metallic zinc and freshly ignited zinc oxide. The conditions being :—Bulk, 200 c.c.; acidity, 2 c.c. concentrated hydrochloric acid; temperature, about 80° C. Uranium acetate was used as an indicator on porcelain. An allowance of 0·3 c.c. was made in each case for the excess necessary to affect the indicator. The results of six concordant determinations gave as the strength of this solution, 1 c.c. = 0·005857 grm. of zinc.

This solution was then used to titrate solutions containing known weights of lead as follows :—

Neutral Solution.—Separate portions of metallic lead, of about 1 grm. each, were dissolved in nitric acid, hydrochloric acid added, and evaporated to complete dryness; the lead chloride was then dissolved in hot water, diluted to 200 c.c., and titrated. The titration in a neutral solution is not altogether satisfactory. Five determinations gave results varying from 0·02454 to 0·02461; average, 0·02458.

Acetic Acid Solution.—Six determinations gave from 0·02450 to 0·02458; the average coinciding with the two most satisfactory titrations is 0·02454 grm.

Hydrochloric Acid Solution.—In a solution containing one drop of concentrated hydrochloric acid, the results were from 0·02441 to 0·02446; average, 0·02444 grm. With 1 c.c. of hydrochloric acid the results were unreliable, on account of the solubility of the precipitate.

Assuming that the precipitates formed are in one case $Zn_3K_2(Fe(CN)_6)_2$, and in the other $Pb_2Fe(CN)_6$, or that an amount of ferrocyanide which precipitates three atoms of zinc precipitates four of lead, the factor by which the zinc standard must be multiplied to give the lead standard is 4·218. This gives by calculation from the zinc standard, 0·0247 as the lead standard of the solution.

The amounts of lead precipitated per cubic centimetre in no case reach this value, and although the variations are not so great as is shown from the analyses of the precipitates, they are in exactly the same order, and so confirm the statement that increase of acidity tends to diminish the percentage of lead in the precipitate.

Our results agree closely with Low's statement (*Journ. Amer. Chem. Soc.*, 1893, xv., 550), that a solution containing 10 grms. per litre of crystallised potassium ferrocyanide will equal 10 milligrms. of lead per cubic centimetre, and are at complete variance with a statement by Furman ("Manual of Practical Assaying," p. 139) that it requires 16 grms. per litre for such a solution. Furman's figure is evidently based on the assumption that this value can be determined by a direct ratio between lead and zinc.

Cadmium Ferrocyanide.

The potassium ferrocyanide solution, already described, was used to titrate a number of solutions containing cadmium under different conditions. Portions of cadmium oxide of 0·3 to 0·4 grm. each were dissolved in hydrochloric acid, and evaporated to complete dryness, then dissolved in 200 c.c. of hot water, and titrated. It was found that uranium acetate on porcelain was very unsatisfactory as the precipitate reacts with the indicator, as is the case with manganese, so that the end tests in these titrations were made on filter-paper, placing the drops so that the precipitate of cadmium ferrocyanide did not come in contact with the uranium acetate.

The results in a neutral solution were not concordant, varying between 0·0071 and 0·00727 grm. of cadmium per cubic centimetre.

In a solution containing 1 c.c. of 50 per cent acetic acid the results ran from 0·00699 to 0·00702 grm. of cadmium; average, 0·0070 grm.

In a solution containing 1 to 2 c.c. of concentrated hydrochloric acid, the average of six determinations on cadmium oxide gave 1 c.c = 0·007177 grm. of cadmium; this was checked by four tests with metallic cadmium, which gave 0·007165 grm., or a general average of 0·00717 grm. Another set was made with only a few drops of hydrochloric acid present; these gave almost the same results. With this solution it was found possible to use uranium acetate on porcelain, but drops on filter-paper are a safer end-point for cadmium titrations.

As cadmium hydroxide is soluble in ammonia it was possible to extend the titration to an ammoniacal solution by using as an indicator a 4 per cent solution of copper sulphate, as recommended by Moldenhauer for zinc (*Chem. Zeit.*, 1889, xiii., 1220, and 1891, xv., 223). The spots are made on filter-paper, as already described; the end-point, a red line, is distinct but not as delicate as with uranium acetate. An allowance of 0·9 c.c. was made for the excess necessary to affect the indicator. Four tests gave the following values for 1 c.c. :—0·00669, 0·00678, 0·00674, 0·00674; average, 0·00674 grm. of cadmium per cubic centimetre.

The formula usually assigned to cadmium ferrocyanide is that given by Hermann (*Ann. Chem u. Pharm.*, 1868, cxlv., 235), $CdK_2Fe(CN)_6$; assuming that this is the composition of the precipitate, the ratio as regards ferrocyanide is $3Zn = 2Cd$, and the strength of the ferrocyanide solution used would be 1 c.c. = 0·00671 grm. cadmium. The results of the titrations do not agree with this value except those obtained in an ammoniacal solution.

Other formulæ have been given for cadmium ferrocyanide. Dammer gives it the normal composition $Cd_2Fe(CN)_6$, and cites Wittstein (Büchner's *Repertorium der Pharm.*, lxiii., 316—317) as his authority, but the original article gives neither formula nor analysis.

Wyrouboff (*Ann. Chim. Phys.*, 1878, [5], viii., 449) gives the composition under all conditions as $K_2Cd_5(Fe(CN)_6)_4$, which has been altered in Comey's "Dictionary," so as to satisfy the valence of the $Fe(CN)_6$ radical to $K_6Cd_5(Fe(CN)_6)_4$. Assuming that this is the precipitate formed, the ratio as regards ferrocyanide becomes $6Zn = 5Cd$, and the strength of the solution used would be 1 c.c. = 0·00838 grm. cadmium.

Our results in acid solutions are intermediate between these values, and indicate a variation in the composition of the precipitate between the formulæ of Hermann and of Wyrouboff. They are confirmed by a statement by Mackay (*Journ. Amer. Chem. Soc.*, 1899, xxi., 940) that it requires about 2½ per cent less potassium ferrocyanide to precipitate cadmium than is required by the formula

$CdK_2Fe(CN)_6$, or, in other words, the cadmium standard is higher than would be obtained by calculation. They are again in direct contradiction to the statement by Furman that the cadmium standard can be obtained from the zinc standard by direct proportion assuming that $2Zn = 2Cd$.

In order to ascertain the composition of cadmium ferrocyanide under different conditions analyses of the precipitates must, of course, be made. This work has already been started, and while no results have yet been obtained, the marked difference in the physical properties of the precipitates seems to confirm the variation in composition.

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ON THE

DETECTION AND ESTIMATION OF ARSENIC IN BEER AND ARTICLES OF FOOD.*

By WILLIAM THOMSON, F.R.S.Ed., F.I.C., &c.

Towards the end of last year it was discovered that a danger which was recognised as a possibility had become a reality, viz., that sulphuric acid containing large quantities of arsenic trioxide had been employed for the conversion of starch into sugar, and that such contaminated sugar had been employed in the brewing of beer, with the result that thousands of people in Manchester and the neighbourhood had suffered from more or less acute arsenical poisoning. This calamity led to the examination of beer and the materials employed in its manufacture, and it was for the first time discovered that arsenic must have been during the last century almost always contained in beer in more or less appreciable or poisonous quantities.

Arsenic is present in nearly all malts and hops, and it is introduced by the process of drying which is nearly universally employed. This process consists in placing the sprouted barley (malt) on the floor of a room covered with perforated tiles or wire-cloth, and making a large fire in the room underneath with coke or anthracite coal; these fuels contain arsenic in greater or less quantity, which volatilises as arsenic trioxide, and condenses on the malt. Coke, however, usually contains a much larger quantity than anthracite.

A disease amongst beer drinkers has long been recognised in Manchester and the district (where coke is employed largely for drying malt), as peripheral neuritis, and from its supposed connection with the consumption of beer it has been called also alcoholic neuritis.

It is curious, however, that in Scotland, where presumably as much, if not more, alcohol per head is consumed than in Lancashire, alcoholic or peripheral neuritis amongst whiskey drinkers is almost unknown. This has led to the suggestion that the so-called alcoholic neuritis is really arsenical neuritis.

It has also been shown that arsenic administered along with alcohol is a much more potent poison than when given in the ordinary way medicinally. Under these conditions it becomes exceedingly important that some reliable method should be found for detecting and estimating minute quantities of arsenic in beer or in food.

It has been suggested that large quantities of materials, such as beer, should be treated with sulphuretted hydrogen, and the arsenic separated and determined by direct weighing. This, however, involves a large amount of work, and the results cannot be regarded as satisfactory when determining such minute quantities as, say, the $\frac{1}{70}$th of a grain to the gallon. I have therefore been led to make experiments with a view of finding, if possible, a process which should be simple and reliable for detecting and estimating minute quantities of arsenic when contained in beer and food stuffs. After a large number of experiments I found that the most satisfactory method was to destroy all the organic matter contained in the beer or any article of food by means of nitric acid together with small quantities of sulphuric acid, and after the whole of the nitric acid had been removed by evaporation, to dilute the resulting liquid to a standard volume, and take if necessary an aliquot part of the solution for treatment in the Marsh apparatus, so as to obtain as nearly as possible a mirror of minimum standard intensity on the heated tube through which the hydrogen is passed. By this means very reliable approximate estimations of the quantities of arsenic up to the $\frac{1}{100}$th of a grain per gallon of beer or per pound of food may be made when other conditions are fulfilled, and when working on 50 c.c. of liquid or on 5 grms. of solid, the chief of which is that sulphuric acid freed from arsenic by distilling with chromic acid should be employed along with zinc, which is practically chemically pure, and which is not readily acted upon by dilute sulphuric acid, a drop of a pure solution of sulphate of copper being required to start the reaction.

Zinc which is readily acted upon by sulphuric acid, and which gives off gas freely, usually retains some of the arsenic; so that whilst a blank test shows freedom of the zinc from arsenic, it also shows freedom from arsenic when a very minute quantity of that metal is added to the contents of the apparatus.

I have found that mercury in contact with zinc in the Marsh apparatus holds back the whole of any minute quantity of arsenic; magnesium, tin, and lead hold back a large proportion of any minute quantity; whilst aluminium and copper hold back small proportions of minute quantities of arsenic. When the total quantity present in the Marsh flask approaches $\frac{1}{100}$th of a grain, the deposit is liable to take place in two rings of the metal with a space free from any deposit between them. The first ring nearer the flame is crystalline metallic arsenic and of a metallic brown colour; the second ring is of a bluish colour, and is evidently an allotropic modification occurring as fine dust or in flakes. I have prepared considerable quantities of these deposits, and taken their specific gravities. The first has a specific gravity of 5·705, and the second a specific gravity of 4·769. The formation of this allotropic modification as a second ring deposit is extremely inconvenient when estimating minute quantities, as it increases the difficulty of comparing the mirrors obtained, with standard mirrors, and I have spent much time in trying to understand why arsenic should be deposited in this curious manner in two broad rings of different colours, with a space of an eighth to a quarter of an inch quite free from arsenic between them. It naturally occurs to one to ask, what is the law which makes a deposit from a continuous stream of hydrogen containing minute quantities of arseniuretted hydrogen of one form of arsenic behind the heated part of the tube, then that the arsenic liberated by the heat should jump over a considerable space, which is left clear and free from deposit, and, finally, that it should deposit as arsenic of a different colour, and presumably different molecular constitution, in another and separate ring further on? These deposits do not take place in very distinct rings when the hydrogen is saturated with moisture. The separate deposits are most marked when the hydrogen is passed through a single drying tube of chloride of calcium, and it again ceases to be very marked when the hydrogen is excessively dried by passing over strong sulphuric acid and the chlorides of zinc or calcium or other strongly hygroscopic substance; the deposits when the gas is supersaturated with water, or when extremely dry, being distributed slightly and evenly along the tube behind the first brown mirror.

I have ascertained that these second arsenic mirrors are entirely prevented by the presence of a small quantity of the vapours of such bodies as ether, alcohol, petroleum spirit, benzene, or acetic acid, and the arsenic deposited under these conditions is of precisely the same bright metallic brown colour. As these deposits presumably differ from each other by their molecular constitution only, one would expect that the action of these vapours (which do not produce any deposit when they are passed along with hydrogen free from arsenic through glass tubes heated to redness), is also of a purely molecular nature. This bluish coloured arsenic, which exists as a fine powder, when gently heated by a Bunsen flame loses

* Read before the British Association (Section B), Glasgow Meeting, 1901.

its blue colour, and becomes crystalline, and appears to be converted into the first or brown form.

It is an important question which may possibly be settled by the Royal Commission at present holding its inquiry, as to what quantity of arsenic should be allowed to be present in beer; some allege that everything contains arsenic, and one has only to extract from a sufficiently large quantity of any material to obtain evidence of its presence.

It seems to me that if evidence of appreciable quantities of arsenic can be obtained from, say, 50 c.c., *i.e.*, less than a sherry wine glassful of beer, or from 5 grms. of malt or dried food by any test whatever, that such beer or food should be condemned. I must confess that such a standard would condemn the beer from almost every brewery in the country at the present moment. It is impossible to accurately test the beer from every brewing, and as the present method of drying the malt will contaminate it with arsenic to some extent, and it may do so to a serious extent without the cognisance of the maltster. The only practicable method seems to be to insist on the practical absence of arsenic from beer or food by devising methods of drying the malt or preparing the food which will not contaminate it.

I must acknowledge my indebtedness to my assistant, Mr. W. E. Wild, B.Sc.(Vict.), who has aided me by his careful and painstaking work.

THE CLEARING OF TURBID SOLUTIONS AND THE MOVEMENT OF SMALL SUSPENDED PARTICLES BY THE INFLUENCE OF LIGHT.*

By G. QUINCKE (Heidelberg).

Turbid solutions or suspensions (*trube Losungen Trubungen*) I call water, in which many small solid or fluid particles are suspended for a long time. The small particles are visible with the microscope.

Colloidal solutions of doubtful character will be discussed later.

Sedimentation, or formation of flocks (flocking) is observed if small quantities of acid or salt solutions are brought in contact or mixed with the turbid solution.

For instance, the sand-bank at the mouth of a river is the effect of the clearing power of the sea-water on the particles of clay suspended in the fresh water of the river.

Turbid solutions of clay, kaolin, silica, gum-mastic are flocked by so small quantities of acid or salt that the increase of weight by the clearing substance cannot explain the augmented velocity or the flocking of the falling particles, or the sedimentation of the turbid solution.

Franz Schulze (*Poggendorff's Ann.*, 1866, cxxix., p. 366), and Schlœsing (*Comptes Rendus*, 1870, lxx., p. 1345), found 1/10,000—1/100,000 of calcium or magnesium salts sufficient to clear suspensions of clay. Bodländer (*Gött. Nachr.*, 1893, p. 267) has measured the clearing or coagulating power of different salts for suspensions of kaolin; Hardy (*Proc. Roy. Soc.*, 1900, lxvi., p. 111—119) for suspension of gum-mastic; Spring (*Rec. Trav. Duin. des Pays-Bas*, 1900, x., 2 Ser., 4, No. 3, pp. 294, 222) for suspensions of gum-mastic, kaolin, silica; Bodländer found suspensions of kaolin flocked, if the quantity of the added salt has been greater than a distinct, very small quantity; the "*Schwellenwerth*" of the clearing substance. Electrolytes promote, insulators retard the clearing of the suspensions (Barus, *Phys. Bribl.*, 1888, xii., p. 563; Bodländer). The clearing power of a salt depends on the valence of the salt, and the kation of the electrolyte (Hardy, Spring).

According to Hardy (*loc. cit.*), the particles of gum-mastic or heat modified proteid move contrary to an electric current. In presence of a minute amount of barium chloride or free acid, the particles of gum-mastic or heat-modified proteid move with the electric current. At the isoelectric point, for a distinct small quantity of barium chloride or acid, the electric movement vanishes, and coagulation or precipitation occurs.

An explanation of the clearing power of the acids or salts is not given.

In the coagulated solutions I found flocks adhering to the walls of the glass vessels, and many air bubbles divided through the flocks. Both phenomena prove that on the surface of the flocks, at least a short time after formation of the flocks, an oily viscous fluid exists. On the surface of separation of this oily fluid with the surrounding aqueous fluid, a surface tension acts, and air-bubbles are separated as in the limit of two heterogeneous fluids. Probably changes of the surface tension of the boundary of oily and aqueous fluid, and the periodical spreading of heterogeneous liquid, will excite vortices, and join together the small suspended particles to form the flocks. The surface forces are the same as the forces which form foam-cells by the contact of alkaline oleates with water, which I demonstrated at the meeting of the British Association at Oxford, 1894. The flocking influence of so very small quantities of clearing matter is now intelligible.

I shall prove that this explanation is the right one.

Alcoholic solution of gum-mastic gives in a large mass of water many unseen threads and foam-walls, in which are distributed a great many small visible spheres. Copper sulphate added to the water with the mastic-foam moves the foam-walls against the copper sulphate, they become clearer, and are dissolved. The sphere and the foam-walls prove the formation of an oily viscous fluid by the action of water and gum-mastic, which I will call mastic-hydrate, and which possesses a surface tension in the surface of separation with water. The copper sulphate is soluble in water and in mastic-hydrate, has the surface tension zero in the limit with water and in the limit with mastic-hydrate, and must be spread out on the common surface of mastic-hydrate and surrounding water. The spreading excites vortices, and draws the surrounding matter towards the spreading centre, the surrounding fluid is stirred up, a new portion of copper sulphate is brought in contact with the mastic surface, spreads out, and so is repeated in short periods; the spreading of the added salt, the formation of vortices, and the mastic particles are attracted by the copper solution.

The solution of copper sulphate, which is put with a long thin funnel under a turbid solution of mastic in a test-tube, will diffuse in the mastic solution, spread out on the surface of the suspended particles, excite vortices, draw the mastic particles together or against the walls of the test-tube, where they will adhere. The connected viscous matter will flow together and form drops, bubbles, or coherent foam-cells (flocks). On the surface of the mastic-hydrate is collected, as in all new built boundaries of two heterogeneous fluids, the absorbed air in small bubbles; one part of the flocks with the adhering air will rise, the other part with the larger flocks will sink to the surface of the salt solution.

Spreading or vortices of sufficient energy and connection, or flocking of the suspended particles, demands a certain concentration of the copper sulphate, corresponding to the "*Schwellenwerth*" of Bodländer.

Solutions of NaCl, HlC, $K_2Cr_2O_7$, $FeCl_3$ spread out on the surface of mastic-hydrate as with $CuSO_4$, and have the surface tension zero. The coagulation or clearing of mastic solutions by this salt solution is explained in the same way as with $CuSO_4$.

Turbid solutions of kaolin in glass cylinders of 100×10 c.m. form a series of horizontal layers having about the same distance. After two months a great many flocks adhered on the shadow side of the glass. Under the microscope the flocks showed threads or tubes of a downward flown liquid, with spheroidal enlargements

* Read before the British Association (Section A), Glasgow Meeting, 1901.

or contractions (*Anschwellungen und Einschnürungen*). The sediment on the ground of the glass cylinder had the appearance of solidified liquid, contained deformed bubbles and coherent foam-cells, smooth spheres of 0·002—0·0004 m.m. diameter, with greater refraction than the neighbourhood.

The particles of kaolin have been covered by the influence of the water with an oily, viscous fluid, probably silica hydrate, on the surface of which another fluid has been spread out. The periodical spreading has combined the suspended kaolin particles in larger flocks, which slowly have been sunk to the ground, or were drawn by the vortices against the glass walls where the particles covered with oily fluid adhered. The oily silica hydrate has formed spheres, bubbles, or coherent foam-cells, and has been afterwards solidified.

Turbid solutions of 1/1000 kaolin give in test-tubes solutions over $CuSO_4$, $FeCl_3$, $CaCl_2$, or $Ca(HO)_2$ foam-flocks with thin walls, in which many little grains are distributed, or with thick foam-walls, in which again small chambers or cells with thin walls are enclosed. The flocks of kaolin adhered to the glass wall, so have been built in the beginning by viscous fluid.

Also over solutions of sugar, solutions of kaolin have formed two thick flock-layers.

Turbid solutions of potash soap have shown flocks over chloroform, sulphide of carbon, aqueous solution of sugar, $CuSO_4$, ClH.

Turbid solution of oleic acid has been flocked by solutions of ClH, $CuSO_4$, or chloroform, sulphide of carbon, and sugar. Turbid solution of China ink by solution of $CuSO_4$ and ClH.

The order of the flocking solution, governed by the velocity of the clearing, changes with the concentration of the suspended particles.

Electrolytes and insulators may be clearing substances.

The flocks of mastic and kaolin adhered to the shaded side of the glass wall by the artificial clearing by means of the light.

The views of Barus, Hardy, and Spring on the clearing power of different liquids, especially of the electrolytes, are not confirmed by my experiments. It is not proved that the kation of the clearing electrolyte is the clearing matter.

The flocks of gum-mastic in the turbid solution, are formed by a thin layer of mastic salt solution (*Mastixhaltiger Salzosung*), which is connected to the surface of the mastic particles by molecular force. This thin layer of mastic salt solution will develop to sensible electromotive force in contact with the pure salt solution outside, and no movement of the suspended particles with the thin layer by an electric current will be possible. My theory explains the theory of the flocks and of the isoelectric flocks of Hardy, which are not moved by the electric current. The process of clearing is the same in all turbid solutions. All flocked particles, or in suspended particles united in flocks, are covered with a thin layer of solution, nearly isoelectric with the surrounding pure salt solution, and cannot be moved by electric forces.

If by the influence of light more spreading fluid is formed on the light side than on the shaded side of the suspended particles, the suspended particle will go towards the light. I will call this phenomenon positive photodromy.

If the influence of light would stop the formation of the spreading solution, or the spreading film, the flocks would go to the shaded side, or would show negative photodromy.

A retarding influence of the light is not probable, but many physicists suppose with E. Becquerel that there is a retarding or stopping influence of red light, on the fluorescence of Sidot's blende. I think that the negative photodromy may also be explained by the heating effect of the light, and the formation of air-bubbles on the light side of the suspended particles. The air-bubbles will hinder the spreading of the newly formed solution on the surface of the suspended particles, and the vortices of sufficient energy will only exist on the shaded side; the flocks will go away from the light, or show negative photodromy.

The Stability of Turbid Solutions.

Turbid solutions of gum-mastic, silica, sodium or potassium silicate, kaolin, gummi-gutti, shellac, soap, proteid, can remain apparently unchanged for months or years, but after some weeks or months we can always find flocks on the bottom of the solution.

Moreover, horizontal layers are formed with more or less suspended particles. What is the reason of the stability of the turbid solution? Hardy and J. J. Thomson see the reason for the stability in the electromotive force on the boundary of the suspended particles and the surrounding fluid, which hinders the movement of the solid particles, while, according to Dorn, electric work is done by the displacement of the particles. The action is the same as if the viscosity of the fluid has been increased.

That electric work is done by the displacement of suspended particles, or by the displacement of fluids over the solid walls of porous bodies, and that electromotive force exists at this boundary, has been known before the researches of Dorn, and is a consequence of my old researches on capillary electric current. If the explanation of Hardy and J. J. Thomson be right, the turbid solutions must have the greatest stability, if the suspended particles show the greatest electromotive force in contact with the surrounding fluid, *i.e.*, sulphur, silica, shellac suspended in water, but shellac gives turbid solutions of little stability. It may be that the electromotive force at the boundary of liquid and suspended particles may increase the stability of the suspension, but the principal reason of the stability may be that the velocity of the falling particles is not constant, but variable or periodic. The impulses of the periodic velocity are propagated with the velocity of sound, and will be reflected inside or at the bottom of the turbid solution. The direct impulse will interfere with the reflected impulses, and the particles will be collected in horizontal layers at distances of half a wave-length.

The air also separated at the common surface of the suspended particles and the surrounding liquid has in many cases an important influence, and will be attached to it or will cover it. The diameter of the air-bubbles or thickness of the thin air cover may be so small that it is not possible to see it with the best microscope, but it forms the condensation nuclei for former separated masses of absorbed air.

In turbid solutions of gum-mastic, soap, or oleic acid one may see these air-bubbles. In turbid solutions of kaolin or silica they act as a Cartesian diver; the suspended particles and the layers of particles rise if they are lighted up by sunshine, and sink again in the shadow by a change of density or volume of the air.

MONAZITE FROM NEW GRANADA.

By NICHOLAS J. BLUMAN.

THE following is a recent analysis of a sample of monazite from New Granada:—

Cerium oxide, Ce_2O_3	25·02
Lanthanum oxide, La_2O_3	22·41
Thorium oxide, ThO_2..	18·00
Manganese oxide, MnO	1·21
Calcium oxide, CaO	2·13
Tin oxide, SnO_2	3·00
Phosphoric acid, P_2O_5	28·23
Iron, Zinc, Sulphur	traces
	100 00

The specific gravity of the mineral is 6·001, hardness 5, colour reddish-brown.

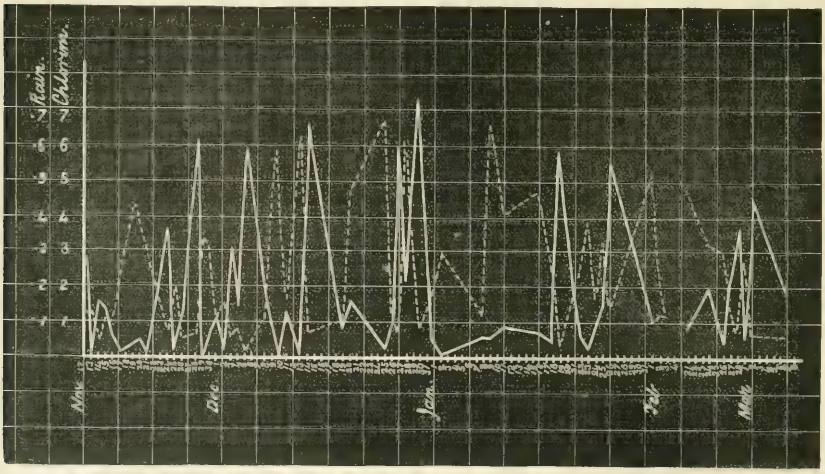
ON THE INVERSE RELATION OF CHLORINE TO RAINFALL.*

By WILLIAM ACKROYD, F.I.C.

ROBINET and other French observers have shown that the early portions of a shower contain more fixed matter in solution than those subsequently collected (Smith on "Air and Rain," p. 268), from which it follows that on the same day there must exist an inverse relation between the amount of matter in solution and the quantity of rainfall.

Collecting various parts of a shower, however, is inconvenient as involving too much labour, and would, moreover, only accentuate the apparently erratic differences which exist when rainfalls of various dates are compared among themselves, for which reasons probably observers have generally been satisfied with monthly or half-yearly averages. The writer finds that when the periods of observation are shortened to daily estimations, say, of the chlorine, it clearly appears that minimum amounts of rainfall are marked by maxima of chlorine contents, and *vice versâ*. Thus, in a daily comparison where the results are plotted for tenths of an inch of rainfall and parts per 100,000 of chlorine, the respective curves interlock, and each chlorine peak has its corresponding rainfall hollow. This will be seen on following the plotted observations in the diagram for Halifax, November 12th, 1900, to March 7th, 1901. It is also apparent in the diagrams for country rainfall, which illustrate my paper "On the Distribution of Chlorine in Yorkshire," Part II., and where the observations are weekly. Regarded as a method of research it will be found that marked parallelism of chlorine curves, where several are compared for the same times, and widely separated areas, may be looked upon as being due to common causes; as, for example, the atmospheric transportation of salt from the sea, or the spreading of the great smoke cloud of manufacturing centres.

* Read before the British Association (Section B), Glasgow Meeting, 1901.



——— Rainfall, in tenths of an inch.
..... Chlorine, in parts per 100,000.

ON THE ABSORPTION OF AMMONIA FROM POLLUTED SEA-WATER BY THE *ULVA LATTISSIMA*.*

By Prof. LETTS, D.Sc., Ph.D., and JOHN HAWTHORNE, B.A.

IN a previous research (*B.A. Report*, 1900, and *Proc. Roy. Soc. Edin.*, 1901, p. 268), it was shown that the occurrence of this sea-weed in quantity in a given locality is associated with the pollution of the sea-water by sewage, the evidence being of three kinds:—(1) The high proportion of nitrogen contained in the tissues of the *ulva*; (2) an examination of certain localities in which the sea-weed occurs in abundance, and of others from which it is virtually absent; and (3) experiments on the assimilation of nitrogenous compounds by the growing *ulva* from sea-water artificially polluted.

Commencing these latter experiments somewhat cautiously, it was first proved that all the ammonia was removed from a sample of sea-water considered to be somewhat highly polluted (0·046 part ammonia per 100,000) by a few days' contact with the sea-weed. Next, it was found that the absorption occurred in less than twenty-four hours, while later experiments have shown that the remarkable power of assimilating ammonia which the sea-weed possesses had been altogether underestimated, as well as the rapidity with which the absorption occurs. The method of experiment was that previously employed. A sample of the polluted sea-water was first analysed and placed in a glass dish. Next a frond of the *ulva* was immersed in it, and, finally, portions of the sea-water withdrawn and again analysed after suitable intervals. Two different series of experiments were made, the first with a solution of ammonium chloride in pure sea-water, and the second with a mixture of sea-water and the effluent resulting from the treatment of sewage by the so-called "bacteria beds." All the experiments in the first series were made with the same piece of sea-weed, which had an area of about 200 square inches; and a

* Read before the British Association (Section B), Glasgow Meeting, 1901.

similar remark applies to the second series, in which, however, several pieces of sea-weed were used, having a total area of about 600 square inches. Individual experiments in both series were made to test the absorptive power of the *ulva* in relation to concentration (of the ammonia), as well as the effects of light and darkness. The following table gives the chief results obtained :—

Absorption of Ammonia by Ulva latissima *from*—

Solution of Ammonium Chloride and Sea-water.
(Area of Fronds 200 square inches).
(Volume of Mixture, 2½ litres).

No. of Expt.	Parts of Ammonia per 100,000 of liquid originally present.	Percentage of Ammonia absorbed after Hours— 1.	2.	3.	4.	5.	In
1A	0·085	59	81	91	—	—	Daylight.
5A	0·180	58	88	96	97	—	
4A	0·085	37	77	87	91	—	Darkness.
7A	0·960	29	44	56	67	75	

Mixture of Bacteria Bed Effluent and Sea-water.
(Area of Fronds 600 square inches).
(Volume of Mixture 2½ litres).

1E	0·084	64	82	91	—	—	Daylight.
6E	0·412	59	86	96	98	99	
3E	0·080	18	45	58	—	—	
4E	0·095	58	79	87	94	96	Darkness.
8E	0·532	43	63	73	90	—	

The general conclusions to be drawn from the experiments are as follows :—

(1). The absorption of ammonia by the sea-weed is very rapid, and with the mixtures used practically all the ammonia was absorbed in five hours (with one exception, when 75 per cent was lost).

(2). The amount absorbed is greatest during the first hour of contact, and then rapidly falls off.

(3). Although the concentration of the ammonia exercises some effect on the proportion absorbed, it is by no means so considerable as might have been expected.

(4). The sea-weed absorbs ammonia both in daylight and in darkness, but the proportion in the latter case is rather less than in the former.

(5). The effects of an increased area of the sea-weed on the proportion of ammonia absorbed are not so great as might have been expected.

These results may be of practical importance in those districts where a serious nuisance results from the decay of large quantities of the *ulva* which have been washed ashore, or which have accumulated in shallow water. For it seems probable that by allowing the effluent from the bacterial treatment of sewage (which treatment gets rid of much of the ammonia originally present) to remain in contact with the growing *ulva* in specially constructed ponds containing sea-water, before discharging it into the sea itself, the ammonia or nitrate will be absorbed, and that the mixture of effluent and sea-water will then no longer provide nourishment for the *ulva* in the sea itself, and that, consequently, the sea-weed will be so much reduced in quantity in the district as to cease to give rise to a nuisance.

The stimulating effects of the ammonia or effluent were evident from the rapid evolution of oxygen from the surface of the sea-weed, which always occurred about fifteen minutes after the addition of the polluting substance, and forms a pretty experiment.

In two cases the dissolved gases were extracted from the sea-water in which the *ulva* was immersed (by boiling out with dilute sulphuric acid *in vacuo*) immediately after adding the polluting material, and again some hours later, and analyses made. The following results were obtained :—

Experiment 5A (*Daylight*).

	Immediately after adding Ammonium Chloride. (·180 part per 100,000). (C c. per litre at N.T.P.).	Four Hours later.
	T = 14·4.	T = 15·9.
CO_2	21·69	15·90
O_2	11·41	14·84
N_2	9·79	9·88
	Loss of CO_2 = 5·79 c.c.	Gain of O_2 = 3·43 c.c.

(About 2 c.c. of evolved oxygen gas were also collected).

Experiment 8E (*Darkness*).

	Immediately after adding Effluent. (20 per cent).	Four Hours later.
	T = 14·6.	T = 14·8.
CO_2	63·59	66·44
O_2	6·31	3·85
N_2	11·90	11·74
	Gain of CO_2 = 2·85 c.c.	Loss of O_2 = 2·46 c.c.

In 5A the *ulva* had been in contact with the sea-water for a considerable time, whereas in 8E fresh sea-water was used.

The above analyses are interesting in several ways. First, in Experiment 5A, the amount of oxygen found is greatly in excess of the value given by Dittmar in the *Challenger* Reports for the volume of oxygen which one litre of sea-water can take up when saturated with constantly renewed air at the existing temperature, Dittmar's figure for 15° C. being 5·83 c.c. The action of the *ulva* is therefore, in a sense, to *supersaturate* the sea-water with oxygen under the existing conditions.

Secondly, the amount of carbonic anhydride found (in the same experiment) is much less than that present in normal sea-water, Dittmar's average for the total volume in sea-water being about 48 c.c. per litre, of which in all probability some 40 c.c. are in the form of soluble bicarbonate of calcium or magnesium. It is evident therefore that the *ulva* gains its carbon from the carbonic anhydride of these salts.

Thirdly, the results of the experiment in darkness demonstrate in an interesting manner the true respiration of the *ulva*, carbonic anhydride being evolved in practically the same amount as the oxygen disappearing.

THE EQUILIBRIUM LAW AS APPLIED TO SALT SEPARATION AND TO THE FORMATION OF OCEANIC SALT DEPOSITS.*

By E. FRANKLAND ARMSTRONG, Ph.D.

The paper dealt with the application of the equilibrium law to the problem presented by the progressive separation of salts from solution, which is of special interest in discussing the formation of deposits of potash and other salts formed by the gradual drying up of ancient seas. The method was described of constructing models and diagrams representing the successive changes observed on concentration of solutions containing several inorganic salts.

For any given solution, *e.g.*, sea-water, it is possible from these models and diagrams to forecast the order in which the salts would separate from it on concentration, and also the relative amounts deposited at any stage. It was pointed out how the results obtained in this manner agreed almost exactly with the order and nature of the celebrated natural potassium magnesium salt deposits met with at Stassfurt.

* Abstract of a Paper read before the British Association (Section B), Glasgow Meeting, 1901.

CONTRIBUTIONS TO THE SCIENCE OF THE NITROCELLULOSES.*

By G. LUNGE and J. BEBIE.

(Continued from p. 167).

THE results of Thomas's test are analogous to those of the Abel test; in this also the product arising in the presence of nitrous acid gives the more favourable result.

It is worthy of note that, on repetition of the stability tests with the same material, the time period up to the beginning of the reaction becomes continuously greater. It would be expected that the repeated heating to 80° would rather have decreased the stability. The cause of the opposite result must be due to a slight diminution in the percentage of nitrogen in each sample tested, in consequence of which the explosiveness is lessened.

Experiment 2.—Two nitrations under similar conditions were again carried out. The one nitration mixture was free from nitrous acid; the other contained 0·28 per cent. The treatment of the nitration products was the same as in the previous experiment, only with this difference, that, on renewing the boiling water, the cotton liquid was poured through a filter, as the increase should be determined at this point also. In Experiment 1 this was omitted; there the material was simply poured on to a filter with fine holes, and, after the boiling was over, it was still quite white. In Experiment 2, however, the products gradually became brownish in colour, and after each washing upon the filter, at the renewal of the boiling water a small quantity of a brown substance collected beneath on the filter. In the stability test, the test-papers were deeply coloured after three minutes. This bad result could only be traced to the presence of the brown substance. Both products were boiled again for a few times with water; in this case using the pump without filter-paper at each change of water, by which means the brown substance was removed in the washing. It was so small in quantity that an analysis was impossible, added to which it further contained white filaments from the gun-cotton. It could only be determined that this substance decomposed on ignition at 198° without effervescence, and showed itself insoluble in dilute acetone, and is therefore not identical with the product that, according to Lenk and Cross, causes the instability of gun-cotton. In any case, the formation of this substance has no connection with the nitrous acid, since it occurred in both products.

The material was now again absolutely white, and showed sufficient stability. In order to obtain a better conclusion as to the reliability of the test samples, two series of experiments were carried out, and in the same manner as in Experiment 1.

Thus, a diminution of the stability of gun-cotton through nitrous acid cannot be proved from these two series of experiments. Both products give coincident results in the stability tests. As in Experiment 1, the explosion-point of the gun-cotton obtained from the nitration mixture containing nitrous acid lies from 0·5° to 1° lower; but this slight difference leads to no satisfactory conclusion.

Both series of experiments afford coincident results, which is a proof that, by following exactly similar treatment in both cases, comparable values may be obtained.

With regard to the percentage of nitrogen, no difference of importance was registered. The determinations were carried out after completion of the boiling. Product *a* gave a nitrogen content of 208 c.c. NO; *b*, that of 208·8 c.c. But, before, on using a nitration mixture of 3 parts concentrated sulphuric acid and 1 part concentrated nitric acid, 213—214 c.c. NO was obtained; therefore, during the protracted boiling, the percentage of nitrogen must have become lowered. According to Guttmann, this also occurs in the manufacture of gun-cotton. In a research of Bruley's, on the other hand, after two hundred and sixty hours' boiling, the nitrogen content was only diminished by about 1 c.c. As in our case the material was cut up as finely as possible, it is possible that isolated filaments may have been thrown up on the sides of the vessel during boiling, and thus become over-heated. The same cause may perhaps be attributed to the formation of the previously-mentioned brown substance which diminishes the stability.

The determination of the increase was omitted for the reasons already mentioned, more especially as Lunge and Weintraub have already proved that it is not diminished even through an excessive proportion of nitrous acid, such as never occurs in practice.

From the above, we believe to have proved finally that,

FIRST SERIES.

Day of the experiment.	Without nitrous acid.		With nitrous acid.		Check experiment.
	a_1.	a_2.	b_1.	b_2.	*c*.
7/1/1900	15′ E.P. = 186·5° *t* = 4′ 1″	14′	17′ E.P. = 186° *t* = 4′	18′	15′ E.P. = 199° *t* = 5′ 40″
26/1/1900	37′	40′ E.P. = 186° *t* = 4′ 42″	41′	47′ E.P. = 185·5° *t* = 4′ 40″	15′
3/3/1900	48′ E.P. = 190° *t* = 3′ 30″	47′	45′ E.P. = 188° *t* = 3′ 34″	51′	14′

Temperature of water-bath = 80°.

SECOND SERIES.

5/1/1900	15′ E.P. = 186·5° *t* = 4′ 26″	13′	15′ E.P. = 186 *t* = 4′ 25″	12′	16′ E.P. = 201° *t* = 4′ 20″
3/2/1900	36′	34′ E.P. = 186·5° *t* = 5′ 2″	34′	35′ E.P. = 185·5° *t* = 5′	15′
13/3/1900	47′ E.P. = 191° *t* = 3′ 5″	49′	51′ E.P. = 190·5° *t* = 3′ 4″	56′	15′

* *Zeitschrift für Angewandte Chemie*, 1901, Heft 20.

for the manufacture of gun-cotton, the presence of nitrous acid in the nitric acid is of no significance. It may be again mentioned that our researches were carried out with pure cotton freed from fatty matter. The result thus obtained cannot, of course, without addition, be applied to the manfacture of nitroglycerin. From the great technical value of this question, a decision of this case also would have been desirable; but, unfortunately, the manipulation being considerably more difficult and dangerous than that of gun-cotton compelled us to abandon this research in a students' laboratory.

(To be continued).

ON THE EXISTENCE OF A NEW ELEMENT ASSOCIATED WITH THORIUM.*

By CHARLES BASKERVILLE.

ALMOST five years ago I attempted to separate thorium quantitatively from a neutral chloride solution by saturation with sulphur dioxide and boiling. As may be recalled, this was merely an application of the method formerly made known by me and used in the separation of zirconium (CHEMICAL NEWS, lxx., 57; *Journ. Am. Chem. Soc.*, 1894, xvi., 475) and titanium (*Journ. Am. Chem. Soc.*, 1894, xvi., 427). The separation of thorium by this means was not quantitative. On re-solution of the precipitated portion in hydrochloric acid and exact neutralisation with ammonium hydroxide and treatment again with sulphur dioxide, almost complete precipitation resulted, showing that the initial partial precipitation was not altogether due to imperfect action of the precipitant or the solubility of the basic thorium sulphite† in the neutral menstruum. This was verified by many repetitions of the process, using thorium chloride solutions of different strengths, and varying amounts of ammonium chloride.

These solutions were first made upon fairly pure thorium salts, prepared by me from oxides obtained from analyses of many monazite sands for the North Carolina Geological Survey (*Bulletin* 9, "Monazite and Monazite Deposits in N. C.," 1895). As this conduct was unexpected, and not in keeping with the observed reactions of the group, the experiments were repeated with thorium compounds obtained from different sources, with like results. I was favoured with several grms. of thorium sulphate prepared by Professor Dunnington, of Virginia, from monazite sand found in Amelia County, Va. Prof. Dennis, of Cornell, kindly gave me 3·5 grms. thorium nitrate (99·6 per cent pure); the hydroxide from which it had been prepared was separated by means of potassium hydronitrate (*Journ. Am. Chem. Soc.*, 1896, xviii., 947). I worked up about 5000 litres of thorium sulphate solution, obtained from Carolina monazite kindly collected by the late Mr. H. B. C. Nitze, Assistant State Geologist. The procedure followed need not be detailed here, as it will appear in a subsequent and more extended communication. Finally, Dr. Waldron Shapleigh generously gave me 2 kilogrms. of the purest thorium oxalate to be had at the Auer Welsbach Works. My thanks are due these gentlemen for their kindness.‡

The purest thorium compounds were re-purified by the following procedure:—The sulphate was taken up in cold water, treated with sodium sulphate, and allowed to stand from twelve to twenty-four hours to ensure separation of the remaining cerium salts, the percentage of which was quite small. The liquid was filtered and the hydroxide precipitated in tall cylinders by large excess of chemically pure sodium nitrite. This precipitate was washed by decantation from six to ten times, using twenty volumes (to one of precipitate) of distilled water each time. To remove the last of the sodium salts and other soluble impurities, the precipitate was then dissolved in hydrochloric acid and re-precipitated by slight excess of ammonium hydroxide, and washed by decantation at least ten times, using twenty volumes of distilled water.

I. *Variation in Specific Gravity of the Oxide.*

The determination of the specific gravity of the oxides affords a rapid and excellent means of judging the rate of fractionation and, in a measure, the purity of the rare earths. This method has been especially urged independently by Muthmann and Böhm (*Ber. d. Deut. Chem. Gesell.*, xxxiii., No. 1; CHEMICAL NEWS, lxxxi., 181), as having time advantages over the necessarily long and often tedious equivalent determinations. Brauner also uses the method. The oxide obtained by prolonged ignition with the blast of the purified hydroxide obtained above had a specific gravity of 10·1 corrected to 4° C. Clarke, in his "Constants of Nature" (*Smithsonian Institution*, 1888, Part I., p. 48), gives the following values:—

Name and formula.	Sp. gr.	Authority.
Thorium dioxide, ThO_2	9·402	Berzelius (*Pogg. Ann.*, xvi., 385).
	9·21	Nordenskiöld and Chydenius (*Jahresb.*, xiii., 134).
	9·077 9·200	Chydenius (*Jahresb.*, xvi., 194).
	9·861	Nilson and Petterson (*Comptes Rendus*, xci., 232).
	17° 10·2199 (*a*) 10·2206	Nilson (*Ber.*, xv., 2536).
	15° 9·876	Troost and Ouvrard (*Comptes Rendus*, cii., 1422) (*b*).

(*a*). Reduced to 4° C., this value is 10·201.
(*b*). Clarke gives a note stating that Nilson's determination is the only one of value.

About 10 grms. of the purified hydroxide obtained above were again dissolved in hydrochloric acid, made up to about 300 c.c., and exactly neutralised by dilute ammonium hydroxide. To ensure neutrality, the ammonia was added until the slightest permanent precipitate remained after stirring the cold solution vigorously for five minutes. The precipitate was separated by filtration, and the solution saturated with freshly-prepared and washed sulphur dioxide. Within a few minutes, a flocculent basic sulphite began to separate. As the reaction continued in the cold, the precipitate increased and then decreased somewhat. The solution was filtered cold and the filtrate

* Presented at the Denver Meeting of the American Chemical Society, August 27, 1901.

† These basic sulphites are being investigated at present. It may be well to state that, in addition to a flocculent basic sulphite, there has been obtained a gelatinous compound, or hydrogele, similar in appearance to the zirconium sulphite described by Venable and Baskerville (*Journ. Am. Chem. Soc.*, 1895, xvii., 448).

‡ While in the midst of re-purifying the compounds from such various sources, and desiring to leave no stone unturned in the investigation, during the fall of last year I wrote Prof. Bohuslav Brauner, of Prague, of my observations, and requested a small amount of the purified thorium compound used by him in his excellent work on the atomic weight of that element (*Journ. Chem. Soc. Trans.*, London, 1898, lxxiii., 951). Very likely the letter went astray, as I have received no reply. I was surprised, therefore, to observe in the *Proceedings* of the London Chemical Society (April 10, 1901) an article by him on "Contributions to the Chemistry of Thorium," in which he gives good evidence of the complexity of thorium, dividing that element into Th$_A$ and Th$_B$. Immediately at my first opportunity (April 23rd), at the Spring meeting of the North Carolina Section of the American Chemical Society, I made public mention of my work, which had been discussed in private often with others. Brauner's results were obtained by hydrolysis of the hepta-hydrated thorium tetrammonium oxalate. This communication contains, in part, the results of my experiments reported then and some observations made since. As soon as the unexpected properties were noted, almost five years ago, I indicated the differences by terming one Th and the other Th(X). It is deemed well to make this explanation in presenting a preliminary paper on incomplete work, as it was done independently, and the problem attacked in a different way. Results have been obtained which corroborate Brauner's work. It may also be stated that large quantities of the materials are being worked up, and the work will be pushed to a finality.

boiled, giving a second—but much smaller—precipitate, similar to the first; showing that the precipitate is soluble to some extent in the cold sulphurous acid solution. The hot filtrate was then precipitated with slight excess of ammonium hydroxide and filtered off. Portions of the sulphite and ammonia precipitates were removed from the funnels (care being taken that they were not contaminated with the ashless filter-paper), ignited in platinum crucibles with the blast, and the specific gravity of the oxides determined.

Before treatment	10·1
Sulphur dioxide precipitate	9·58
Soluble portion precipitated by ammonia	10·367

(All determinations here and elsewhere in this paper were corrected to 4° C.).

Twenty grms. of Shapleigh's purest thorium oxalate were re-purified according to the method given above. A saturated solution of chemically pure citric acid was prepared, and the pure hydroxide added in excess, *i. e.*, until no more was dissolved cold when the stirring had continued (by means of a motor) for from twelve to fifteen hours (different experiments). In attempting to concentrate the filtered solution by heat, a heavy white precipitate—resembling, in a measure, barium sulphate in appearance—came down. The utmost care was necessary in boiling the solution, as the bumping was often quite violent. The precipitate re dissolved when the solution was cooled. In evaporating the solution on the water-bath, the precipitate appeared and was dissolved again on cooling.

A thorium citrate is described by Chydenius (*Pogg. Ann.*, 1863, cxix, 55: "Kemisk undersölening af Thorjord och Thorsalter," Helsingfors, 1861), but he did not investigate it further than to determine the percentage of oxide present. The investigation of this citrate, not previously noted, is well under way, and will be published later as a separate paper. For our purpose here, it suffices to state that the precipitate may best be obtained and separated by diluting the solution from five to ten times, and holding it at—or just below—100° C. This has been done by placing the large beaker (Jena glass) in a boiling water-bath for an hour. The precipitate settled well, and the clear supernatant liquid was decanted; the precipitate was washed several times with boiling water by decantation, the settling occurring while the beaker was surrounded by boiling water. Finally, the precipitate was thrown upon a large filter-paper and washed several times with boiling water, or until the wash-water was only faintly acid to litmus. The precipitate was carefully removed from the funnel, avoiding contamination with fibres of the filter-paper, brought to a constant weight at 105° C. in an air-bath. Prepared thus, the body is a beautiful white heavy amorphous powder, and is a hydrated citrate of the real thorium.

Portions of this purified citrate made at different times were ignited in platinum crucibles with blast and the specific gravity of the oxides determined.

Amount oxide taken.	Sp. gr. corrected to 4° C.
0·1989	9·254
0·6000	9·253
0·3830	9·210
0·4166	9·188 (*a*)

(*a*). Citrate prepared from second heating of one of the solutions which was not completely precipitated at first.

From these determinations, it appears that Nordenskiöld and Chydenius very likely at one time had the nearly pure thorium compound. I am inclined to the opinion that the oxide obtained by me above is still not quite pure, for reasons given below (see also "Radio-active Experiments"). One of the regrettable features of the paper is that I am unable yet to submit the results of the spectroscopic investigation of the material. Preliminary atomic weight determinations have been made from this oxide, however.

The filtrates (without the wash-water) obtained from the citrate mentioned above were concentrated in platinum on a water-bath. As the solution became concentrated, a little more of the insoluble citrate separated out, but in one series of the experiments no effort was made to separate it, but the whole carried down to a thick syrup and allowed to cool, when it became a mass of solid crystals, more or less opaque from the insoluble citrate bound up with the mass. Two grms. of this material were ignited, and the specific gravity of the oxide determined.

Oxide taken.	Specific gravity.*
0·4000	10·50

A larger quantity of the saturated citrate solution was prepared, and most of the insoluble citrate removed according to the method given. About 2 litres of filtrate (wash-water not included) were concentrated to 400 c.c. in platinum on the water-bath, when a crystalline scum began to form. The dish was covered and allowed to stand over night. A few heavy crystals separated at the bottom. The thick syrup was drained from the crystals, which, without crushing, were washed three times with water, dried at 120° C. On ignition, 31·61 per cent of oxide was obtained. Specific gravity of the oxide was determined.

Oxide taken.	Specific gravity.
0·1789 grm.	8·77
0·2024 ,,	8·47

What this oxide is I am unable to say, unless it be the new body recently reported by Hofman and Prandtl (*Ber.*, 1901, xxxiv., 1064) as a contamination of zirconium in euxenite. It constitutes only a very small percentage of the thorium, and demands careful investigation, which I cannot at present undertake on account of the wealth of other material demanding more immediate attention. I should like to have the privilege of investigating it later, however.

When the syrup obtained above was further evaporated to about 300 c.c., a white crystalline body separated, and formed a thick coating on the bottom of the dish. The liquid was decanted; the crystals washed until the water was only faintly acid, and dried at 120° C. The residue amounted to 16·20 per cent after ignition, and had a specific gravity of 10·14 using 0·3820 grm. of oxide.

On continued concentration small crops of crystals were obtained, consisting primarily of citric acid with decreasing percentages of oxide. These salts have not yet been closely studied. When the syrup was brought to about 200 c.c., it was diluted approximately to a litre and boiled. A small precipitate, very similar to the first insoluble thorium citrate, yet different, was obtained. The oxide obtained when the material was ignited was exceedingly white.

Oxide taken.	Specific gravity.
0·1812 grm.	11·26

As the quantity of the material obtained was very small, too much weight should not be given to this value.

Two portions of the filtrate from this precipitate were evaporated to dryness in a platinum dish, ignited, and the specific gravity of the residue determined.

	Oxide taken.	Specific gravity.
I.	0·5566 grm.	10·46
II.	0·8316 ,,	10·53

II. was strongly ignited in a covered platinum crucible for three hours.

These determinations prove the presence of an oxide having an unusually high specific gravity, which cannot be accounted for except by the presence of either a new oxide of a known element having greater density than

* Mr. R. O. E. Davis, Assistant in the Laboratory, aided in some of the physical constant determinations. He is at present at work on the citrates and molybdates.

the usual non-volatile residue after ignition, or an unknown element. It is needless to say that the absence of such heavy substances as lead from the reagents was proven. From the variation in the values, assuming no error in manipulation, the oxide is not yet pure; but careful fractionation, using much greater quantities of the material, gives good promise.

II. *Experiments on the Radio-activity of the Oxides.*

In writing of the now well-recognised Becquerel rays M. and Mdme. Curie (*Comptes Rendus*, cxxvii., 175; Chem. News, 1898, lxxviii., 49) say that "the property of emitting rays . . . which act on photographic plates is a *specific property of uranium and thorium*." Sir William Crookes (*Proc. Roy. Soc.*, lxvi., 409) has practically proven that the radio-activity of uranium is due to a constant constituent, which can be partially fractioned out, Ur(X). In the same paper Sir W. Crookes presents the results obtained in a few preliminary experiments he made to separate thorium compounds into an active and inactive body (*loc. cit*). His experiments in fractionating thorium sulphate gave negative results. However, when he obtained six fractions by crystallising the nitrate, the oxide from the first end crystals gave a feeble action, while the other end "gave an impression about three times as intense. This points to the possibility of separating from thorium its radio-active substance" (p. 421). My own experiments are in exact accord with the above. The oxide (9·25 sp. gr.) obtained from the insoluble citrate affects the sensitive plate in the dark after an exposure of seventy-two hours but slightly, while the oxides of higher specific gravity are quite active. A number of plates have been exposed using oxides obtained throughout the research, monazite sand from which the thorium salts were prepared, uranium nitrate, acetate, uraninite, and blanks for comparison. The radio-activity increased with the increase in specific gravity. For reasons given below I am of the opinion that the 9·25 thorium oxide is not quite pure, that is, free from traces of the higher oxide; hence, its faint activity. (See above; method of application is outlined below).

I am not yet ready to assert that the new substance obtained is not the third radio-active body reported by Debierne in pitchblende, actinium (*Comptes Rendus*, October 16th, 1899, and April 2nd, 1900; Chem. News, lxxxi., 169), which he states belongs to the iron group. From Madame Curie's statement, Debierne supposes "that the radio-active property observed in thorium compounds does not belong to this element, but is due to a foreign material," hence actinium? From Rutherford's experiments on induced radio-activity, one is loath to accept the radio-activity of unprotected bodies as sufficient evidence of their sameness. I have not, so far, had time to apply the radiant matter test, but amassing chemical evidence, so far obtained, points to the presence of a hitherto unrecognised body.

An account of the method used in these preliminary experiments on the radio-activity of thorium and its constituents may be of interest. The plan was essentially the same followed by Sir W. Crookes (*loc. cit.*), differing somewhat in details. Placing small circular pill-boxes containing the materials directly on the same sensitive plates was not satisfactory on account of the excessive radiation from the concentrated active body in all directions. Black glazed paper, the size of the plate, was punctured with circular holes about 1·5 c.m. in diameter, and placed dark side up on the plate. A sheet of silver-free lead, about 0·5 m.m. thick, was similarly cut and placed on the paper, which served to protect the plate. The material was placed in quantities varying from 0·25 to 1 grm. in small exhibition glass tubes 1 c.m. in diameter and 5 c.m. tall. These cells were closed by sealing thin circular microscope slide covers to the flange with Canada balsam. After air-drying, the cells were inverted, and the sealed end placed neatly over the circular openings in the lead and paper, thus exposing portions of the plate to the radiant action downward through a thin medium of glass and air, as the cells were not in contact with the sensitive surface nearest the tubes being held up by the flange, which projected beyond the circular opening. To eliminate lateral radiant action, each cell was then surrounded by a cylinder of lead, which was filed to fit snugly upon the sheet lead below. These cylinders were about 2·5 c.m. in diameter inside, and 5·25 c.m. high. Such a battery, having from two to eight cells differently charged, was placed in a box, closed, covered with black glazed paper, several thicknesses of cloth, and locked in a dark room for various lengths of time, twenty-four to one hundred and forty-five hours. The plates were afterwards developed. Similar experiments were carried out, placing the ordinary black paper, usual covering of plates, between the cells and the sensitive surface without puncturing the paper. The active oxides affected the plate through the paper medium.

(To be continued).

THE MEASUREMENT OF GOLD AND SILVER BUTTONS IN QUANTITATIVE BLOWPIPE ASSAYS.*

By JOSEPH W. RICHARDS.

When Harkort, a Freiberg student, invented the quantitative blowpipe assay for gold and silver, in 1824, he was at once confronted with the impossibility of weighing the very small buttons obtained. He surmounted the difficulty by assaying a silver ore repeatedly in the muffle, until he knew with exactness its contents. Then he assayed a standard weight of it by the blowpipe, and obtained a button of a certain size, whose weight was known from the amount of ore taken. Taking half and a third and a quarter of the weight of ore he obtained smaller buttons of known weight. With these he constructed a scale. He drew two fine slightly diverging lines on white cardboard, placed the buttons between the lines at the points where they fitted, and marked opposite those points the corresponding weights, or, rather, the corresponding silver contents of the ore, assuming a standard weight taken for assay.

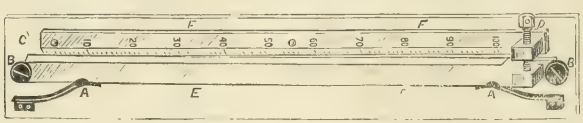
Harkort brought the method to the attention of Plattner, the professor of metallurgy at Freiberg, and published his results at his own expense in a small book entitled "Silverprobe vor dem Löthrohr," Freiberg, 1827.

Plattner took up this method in his regular course of instruction, and improved and extended it. One of his principal improvements was the construction of the button scale rule on ivory, made by the mechanic August Lingke, at Freiberg. To fix accurately the dimensions of this scale, Plattner assayed a very rich silver ore repeatedly in the muffle until it was known with certainty to contain exactly 3·48 per cent of silver. He then made repeated blowpipe assays of this ore, obtaining buttons very close together in size and weight. The two lines were then drawn on ivory so that they diverged approximately the diameter of these buttons in 150 m.m. The buttons were then fitted exactly between the lines, and the point marked 50, the distance from here to the meeting point of the lines being divided into fifty equal divisions. The exact dimensions of the scale as thus made were 156 m.m. from 0 to 50, and the lines 0·9 m.m. apart at 50. The weights corresponding to the various numbers were calculated from the number 50 representing 3·48 m.grms. of silver (when 100 m.grms. were taken for analysis), using the assumption that as the buttons were nearly spheres, or, at least, were homologous in shape, their weights would vary as the cubes of their respective horizontal diameters. The weight of the silver button corresponding to any number from 1 to 50 would be therefore—

$$3{\cdot}48 \times \left(\frac{n}{50}\right)^3.$$

* *Journal of the American Chemical Society*, xxiii., No. 4.

and thus these weights were all calculated and engraved on the scale opposite the numbers. A similar set of weights was obtained in an exactly similar manner for gold buttons. Thus the Plattner ivory scale was devised, and is still used more extensively than any other method of measuring these small buttons.



The defects of the Plattner scale may be enumerated under the heads of:—

1. Errors in construction.
2. Errors in using.

The errors in constructing the scale may be as follows:—

a. The lines are sometimes not mathematically straight.
b. The lines may be rough or ragged.
c. The lines may not meet exactly at the point marked zero.
d. The lines may not be exactly the right distance apart (0·9 m.m.) at the point marked 50.

It is seldom that the best scales made in Freiberg are free from one or more of these defects; I do not believe that more than one out of five is perfect.

The errors in using the scale consist of:—

a. Placing the button too high or too low through optical illusion. The button should be tangent to the inside of the lines, and in a strong light the white metallic surface of the button is difficult to see on its outer edge. One investigator has even proposed putting the silver buttons a short time into ammonium sulphide, so as to blacken them, and thus facilitate their measurement.

b. Placing the button too high by virtue of parallax, which projects the middle diameter of the button against the scale on which it rests, and makes the button seem to fit higher up than its real diameter. The remedy for this is to sight first down one side of the button, then down the other, each time looking perpendicularly to the scale. This operation is tedious, and takes considerable experience.

c. The button being nearly round, it takes considerable time, patience, and experience to get it to a certain spot on a flat surface. This is not an error of the scale, but an unavoidable inconvenience, which becomes accentuated if the ivory warps, so that the scale does not lie level. A beginner will frequently make a greater mistake in measuring a button than in getting it.

Goldschmidt's Method.—Dr. V. Goldschmidt, of Heidelberg, proposed two improvements:—

1. *To Re-melt the Cupelled Buttons on Charcoal.*—This gives to them a more nearly spherical and more uniform shape than is obtained on the cupel. The button is to be removed from the cupel, hammered flat between paper, to clean it, and then touched with the reducing flame, on charcoal, just long enough for it to melt and take the spherical form. Buttons thus re-melted will be heavier than cupelled buttons of the same horizontal diameter, and, therefore, heavier than the given weights on the Plattner scale.

2. *Measuring the Horizontal Diameter of such Re-melted Buttons under the Microscope.*—For this purpose, a divided scale is put into the focus of the eye-piece of a compound microscope magnifying 50 to 100 diameters. A scale of 40 divisions is very suitable, the tenths of each division being estimated when measuring. The buttons are placed on a glass plate, a piece of blue glass gives a nice background, and since they come to rest only on their bases, the horizontal diameter is always in position to be measured. The diameter being known in whole divisions and tenths, reference to a previously constructed table gives the volume and weight of the button, when of gold or silver.

To construct this table, the following ingeniously devised plan was worked out by Goldschmidt:—A number of bits of pure gold are melted on charcoal. The buttons obtained are each measured separately, in divisions on the scale. All the buttons are then weighed together, as accurately as possible. The total weight, divided by the specific gravity of gold, gives the sum of the volumes of the buttons. This latter divided by the sum of the cubes of the separate diameters (expressed in divisions on the scale) gives a function μ. This function is the factor by which to multiply the cube of the diameter of any button to get its individual volume. Expressed algebraically, the above operations are:—

$$\frac{\Sigma \text{ weight}}{\text{Sp. gr. gold}} = \Sigma \text{ volumes.}$$

$$\frac{\Sigma \text{ volumes}}{\Sigma (\text{diam.})^3} = \text{a function} = \mu.$$

Volume of any button $= \mu \times (\text{diam.})^3$.
Weight of a gold button $= \mu \times$ sp. gr. gold $\times (\text{diam.})^3$.
Weight of a silver button $= \mu \times$ sp. gr. silver $\times (\text{diam.})^3$.

From the above data, a table can be constructed showing the weights of gold or silver buttons for every division of the scale up to its full range.

It should be remembered that measurement under the microscope is a very satisfactory laboratory method, but as it requires a compound microscope, it is not suitable for field use or prospector's outfits.

Richards's Scale.—The writer adopts Goldschmidt's idea of re-melting the button on charcoal, wherever practicable, but has devised a modification of Harkort's method for measuring the buttons.

The idea is to make two metallic edges perfectly straight, lying on a flat surface, touching each other at one point, and held apart at the other extremity by a set-screw, so that the point 100 may indicate a fixed width or separation of almost exactly 1 m.m. In reality, the button whose horizontal diameter fits at 100 has a diameter of 1·02 m.m., but this distance has been so chosen that the volume and, consequently, the weight of said button are exactly that of a perfect sphere whose diameter is 1 m.m. The other numbers on the scale have the same significance; for example, the button whose horizontal diameter fits at 43·5 has the volume and weight of a sphere whose diameter is 43·5 hundredths of a m.m., and such is the basis on which the table is calculated.

In using the scale, the button is put into the groove, the scale inclined slightly, and tapped until the button wedges itself. The tenths of a division are estimated, taking the points where the sides of the button touch the scale as the reading. As the button may sometimes roll with its shorter vertical diameter across the scale, several readings are taken, and the highest reading occurring with regularity is the true horizontal diameter. For instance, among 43·4, 43·4, 41·6, 43·5, 41·8, 43·5, it is evident that 43·5 is the horizontal diameter, and 41·6 or 41·8 the vertical. The button can also be observed under the lens, to see how it is lying, at any given reading.

A gentle spring keeps the right-hand strip against the set screw, thus allowing it to be pressed back for cleaning out the slot with a brush or removing a button. The scale is made of hardened aluminum, for lightness, and is set in a velvet-lined leather case. It is made by Williams, Brown, and Earle, of Philadelphia, and sold at the same

price as the imported ivory Plattner scales. P. Stoë, of Heidelberg, makes and sells the scales in Germany.

The advantages of this method of construction over the engraved ivory scale are :—

1. The edges are perfectly straight, from the method of construction.

2. They meet exactly at the zero point, and can be adjusted to the exact distance at 100.

3. The reading is more or less automatic, the errors of placing, parallax, and personal equation being almost entirely eliminated.

The scales are adjusted by the makers, but, if by accident they get out of adjustment, a small rod of wire furnished with each instrument, whose lower end marks a given reading on a correct instrument, provides the means of quick re-adjustment.

Measuring Gold-Silver Alloy Buttons.—When the button obtained is pure gold or pure silver, any of the above methods give its weight directly. If, however, it is an alloy of the two, and is too small to weigh satisfactorily, but must be measured, the question of determining the silver present as well as the gold is a difficult one. The determination is very much facilitated by using the small case of standard alloys designed by Dr. Goldschmidt, of Heidelberg (made by P. Stoë, Heidelberg, imported by Williams, Brown, and Earle, Philadelphia). This is a small tablet in a brass case, containing small flattened buttons of gold-silver alloys, every 1 per cent of silver to 20, then every 2 per cent to 40, and every 4 per cent to 56, where the alloy becomes silver-white. In using, the alloy button to be tested is hammered flat between paper, put on the plate, and examined under the lens by diffused daylight. With a little experience, the button can be placed to one alloy. The observation gives the per cent of silver in the button. Assayers working by the muffle will also find this a very convenient instrument to save parting where a quick, approximate determination is wanted, or to determine how much silver to add to an alloy to get the right proportions for nitric acid parting.

I have classified the different methods available to the blowpipe assayer as follows :—

I. If the button is over 50 per cent of gold, and therefore coloured, melt on charcoal, measure, and note its *volume*. Then proceed by either of the following methods :—

(*a*). Flatten out, compare with the standard alloys, and get the per cent of silver in it. From the table of specific gravities of gold-silver alloys take the specific gravity. Multiply the *volume* of the alloy by its specific gravity; the product is its weight. From the known percentage of silver and gold in it, calculate their respective weights.

(*b*). Melt the button with a button of pure silver having an equal diameter, if the colour of the alloy is pale; or of 25 per cent greater diameter, if the colour is brass-yellow; or of 50 per cent greater diameter, if of nearly pure gold colour. Hammer out flat, and part with nitric acid in the usual way. Wrap the gold in a small piece of pure lead foil, cupel, re-melt, measure, and thus get its weight and note its volume. Subtract the volume of the gold from the volume of the alloy, and the difference is the volume of the silver. The weight of silver corresponding to this volume is obtained directly from the table.

The writer has verified these two methods of procedure, and found them both reliable. The principle of method (*a*) is due to V. Goldschmidt, but not exactly in the simple form given above. The principle of method (*b*) is based on the fact that gold and silver neither contract nor expand in alloying, which fact the writer has verified by experiment and calculation.

II. If the button is less than 50 per cent gold, and therefore silver coloured. Melt on charcoal and note its *volume*. Then proceed by either :—

(*a*). Part with nitric acid (re-melting with more silver if not attacked). Wrap the gold in lead foil, cupel, re-melt, measure, note its weight and volume. Subtract its volume from that of the alloy, getting the volume of the silver, and thence its weight.

(*b*). Measure accurately a pure gold button of approximately the same diameter as the alloy button. Melt together on charcoal, and measure carefully, noting the *volume*. Flatten out (the colour will be yellow), compare with the standard alloys, and, knowing the volume, compute the weight of gold and silver present. The weight of gold found, less the weight of the gold button added, gives the weight of gold in the original assay button. The weight of silver may be obtained by calculation from either the original alloy button or the yellow one after gold had been added.

This method of procedure was suggested by Professor B. W. Frazier, of Lehigh University.

(*c*). Replace on charcoal, and heat intensely in the point of the oxidising flame. The silver slowly volatilises, and in one to five minutes the alloy becomes yellowish. It is difficult to drive all the silver off, as the last 5 or 10 per cent volatilise slowly, and probably also take a little gold with them. It is best to stop when the alloy has a pronounced yellow colour, measure, note the volume, flatten out, compare with standard alloys, and calculate the weight of gold present. Take the volume of that weight of gold from the table, subtract from the volume of original alloy button, and thus obtain the volume and thence the weight of the silver.

The fact that silver can be volatilised from gold in this way, on charcoal, was described by the writer in the *Journal of the Franklin Institute*, June, 1896.

The writer finds methods I. (*a*) and II. (*c*) the most suitable for field work; the parting with nitric acid is preferably a laboratory method, and is the most accurate.

(To be continued).

CORRESPONDENCE.

CHEMICAL NAMES IN BOTANY.

To the Editor of the Chemical News.

Sir,—It may interest some of your numerous readers who may not be aware of the fact, that in the botanical family of the *Melastromaceæ* (established by Jussieu, Bonpland, and Robert Brown), which has been very carefully studied by De Candolle, two genera are dedicated respectively to Lavoisier and Humphry Davy.

None of the plants of this extensive group are natives of our English climate; they are mostly large trees of the hot regions of the globe.—I am, &c.,

T. L. Phipson, Ph.D.

Casa Mia, Putney, S.W.,
October 7, 1901.

OCCURRENCE OF MANGANESE IN WATERS.

To the Editor of the Chemical News.

Sir,—Some little time ago I had occasion to enquire into the cause of a dark brown sediment in a town's water supply, which was giving considerable trouble and inconvenience to consumers.

The first sample which I received was found to contain about 70 per cent of hydrated manganese oxide, the remainder being principally carbonate of lime and organic matter. This result was looked upon with doubt, as the sample had been taken from a source where the contamination of manganese ore, in the form of dust, was not at all impossible. Further samples were then taken right at the very source of the water supply, and these were found to corroborate the existence of manganese in estimable quantities (0·25 grain per gallon hydrated manganese oxide). The water is pumped up from wells in the red sandstone, and is perfectly clear and colourless, and in

every respect a wholesome water. In places down the wells where the water flows over the sandstone there is the same dark brown deposit of hydrated manganese oxide mixed with calcium carbonate, and in pipes which have been laid some years a considerable deposit of the two substances is found.

I have searched in many volumes of the Chemical News and other scientific journals, but can find no record of the occurrence of manganese in waters. Although the amount found in this case is fairly large, it might very possibly have been overlooked in an analysis of the total solids, as compared with the carbonate of lime it would be relatively small.

The manganese appears to exist as a bicarbonate (though this is not certain); it is at once precipitated along with the lime on boiling the solution. When dealing with large quantities, this can be easily seen forming a slight brownish scum on the surface during evaporation.

I venture to trouble you with an account of this experience in the hope that it may prove of interest to some of your readers, and also because it is either an unusual case, or else the occurrence of manganese in waters is apparently overlooked. If a similar case has been noted by anyone, I shall be pleased to compare notes with him. —I am, &c.,

T. H. Byrom.

NOTICES OF BOOKS.

Commercial Organic Analysis. By Alfred H. Allen, F.I.C., F.C.S. Third Edition. Volume III., Part I. *Tannins; Dyes and Colouring-matters; Writing Inks.* Revised and Edited by J. Merritt Matthews, Ph.D. London: J. and A. Churchill. 1901. Pp. 589.

The growth of our knowledge of organic analysis has necessitated a considerable alteration in the arrangement in this new edition of Vol. III., Part I. In the previous edition, this part dealt with the aromatic acids. This subject has now, however, been transferred to another volume, and the one now before us is entirely devoted to tannins, colouring-matters, and writing-inks. These sections have been much amplified, and a great deal of the old material has been re-written. New methods are described, as well as improvements in the old ones. It is to be regretted, as pointed out by the reviser, that our knowledge of tannin analysis is still so uncertain that two methods very rarely give concordant results.

The classification of dyes and colouring-matters has been changed, and the amount of matter given almost doubled; while the method of tabulated reactions adopted must reduce the work of testing by a very great deal.

It is to be regretted that there is rather a long list of errata; many of these may be classed as printers' errors, but some are of real importance—such as for "acid," read "alkali"; for "soluble," read "insoluble."

In a work of this magnitude, it is difficult to pick out any particular points for special notice. The volume teems with valuable information and new methods of procedure. The book is well printed, and bound to match the preceding volume, to which it makes a valuable companion.

The Self-Educator in Chemistry. By James Knight, M.A., B.Sc., F.C.S., F.G.S., F.E.I.S. Edited by John Adams, M.A., B.Sc., Rector of the Free Church Training College, Glasgow. London: Hodder and Stoughton, 27, Paternoster Row. 1901.

The above work is not intended as a preparation for examination, or for students at all in the narrow sense of the term; but recognising the importance of a certain amount of chemical knowledge in every department of life, the author has endeavoured by his book to give a ready means whereby any ordinary person with a desire to become acquainted with the subject can grasp the fundamental principles of chemistry. A number of experiments of simple character are introduced with minute instructions for carrying them out. The author describes his book as an attempt to dispel a little of the "superstitious dread which surrounds the word chemical," an attempt in which we think he has been fairly successful. The first two chapters on the atomic theory and chemical nomenclature are particularly clear, and would be found useful even to students preparing for an examination. Considering that the outlines of both organic and inorganic chemistry are included in 160 pages the subjects are necessarily treated briefly; but the descriptions and explanations are original and clear. There is a table of contents and a good index.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., Nos. 9, 10, and 11.

These three numbers contain no chemical matter.

No. 12, September 16, 1901.

The Molecular Weight of Chloral Hydrate at the Temperature of Ebullition.—M. de Forcrand.—The author applies the rule which he recently discovered (*Comptes Rendus*, vol. cxxxiii., p. 368) to the case of certain compounds which dissociate more or less completely at their boiling point. He first considers the case of chloral hydrate, for which substance the necessary thermochemical constants are almost all known. He admits, as a first approximation, a complete dissociation at boiling point (96·5° C.). M. Berthelot gives the values L = 21990 cal., and S = 5500 cal., from which

$$\frac{L + S}{369{\cdot}5} = 74{\cdot}1.$$

This number, 74·1, is more than double the mean 30, but, assuming the author's hypothesis, this should be the case for two reasons. First, the hydrate has been completely separated into water and chloral; there are now two molecules and the mean value of the quotient ought to be 60. Secondly, the number 21990 cal. is in reality the heat of volatilisation, together with the heat of combination (+6230 cal.); disregarding this latter number, the value 57·30 is obtained, a number comparatively near to 60. The fact of its being too low apparently shows that dissociation is not absolutely total, and this result confirms M. Berthelot's experiments. At the temperature of ebullition the vapour of chloral hydrate contains water, chloral, and a little non-dissociated hydrate.

MEETINGS FOR THE WEEK.

Wednesday, 16th.—Microscopical, 7.30. Exhibition of Mounted Specimens of Marine Zoological Objects, by C. L. Curteis, F.R.M.S. "The Fungi Found on Germinating Farm Seeds," by Miss A. Lorrain Smith.

HARRIS INSTITUTE, PRESTON.

LECTURER IN CHEMISTRY.

The Harris Council invite applications for the Post of LECTURER IN CHEMISTRY. Salary £150. Further particulars may be obtained on application to the Secretary. —Applications, with copies of not more than three recent testimonials, should be sent in on or before Wednesday, October 16th, 1901, addressed to the undersigned.

F. R. JOLLY, Secretary.

THE CHEMICAL NEWS

Vol. LXXXIV., No. 2186.

ON THE DISTRIBUTION OF CHLORINE IN YORKSHIRE.*

Part II.

By WILLIAM ACKROYD, F.I.C.

All figures refer to parts of chlorine per 100,000 of water. As the result of many observations of minima the chlorine is found to increase from 0·7 up to 1, in the west and north-west, where the rivers originate, to 1·7 up to 2 in the east and south-east, where, in the Chalk Wolds, the up-turned edges of the chalk drink in and store up a vast amount of rain water which is utilised by many of the East Riding communities. Beyond this there is a south-eastern area of high chlorine figures formed by the triangular tract of drift ending with Spurn Head; a pump at Paull near the Humber side gave 117·5; a Withernsea well in the drift gravel, 24·4; Hambleton station, 17; Hedon and Ryehill stations, each 16·5. The lowest figure obtained in this area was 2 at Driffield, Hesslewell, and Selby.

Every large centre of population has a high disturbing influence on the normal chlorine for the neighbourhood, which is shown by the chlorine figures yielded by the rain-water. The Massachusetts Board of Health (1890, [1], 680) found that twenty persons per square mile will add, on the average, 0·01 part of chlorine to the water flowing from the district. Such an estimate must have a purely local application on account of the inverse relation existing between the quantity of chlorine and quantity of water, which is pointed out in another paper (Chem. News, vol. lxxxiv., p. 176), and also because of the wide variation of these quantities from various causes. The following is a comparison of the averages for three months winter (1900—1901) rainfall for town and country in Yorkshire:—

Contents of rain-gauge in a manufacturing town (Halifax); average of 51 samples	2·38
Contents of moorland rain-gauges at Widdop, Walshaw Dean, Warley, Ovenden, and Midgley in Yorkshire; average of 68 samples	1·37
Excess of town over country	1·01

That part of the borough of Halifax in which the rain gauge is kept forms a catchment area of 2·03 square miles, and comprises some seven wards with a population of 59,185. Its contribution of chlorine (1·01) through the rain is therefore 0·01 per 288 people per square mile; but the total contribution from air as well as ground in this closely populated district is 0·01 part of chlorine per 53 people per square mile, taking the maximum ground water figure as 5·5. (See *B.A. Report*, 1900, p. 685, and Chem. News, vol. lxxxii., p. 162).

The influence of high winds has direct bearing on the subject. This is shown in plotted diagrams for the three months' observations, where there are two well marked chlorine peaks which synchronise in the four curves, one for the week ending December 24th, 1900, and the other for the week ending January 14th, 1901. In the former week westerly gales prevailed, and presumably the chlorine maximum is evidence of marine influence; the wind acquired its greatest velocity on the 20th December of 43 miles per hour. In the January week strong continuous east winds blew from the German Ocean with a very light rain or snow-fall, a combination again calculated to send up the chlorine to an abnormal height; the highest velocity reached was 27 miles per hour E.N.E. on the 9th, and 25 miles on the 7th January. The velocities are those taken at Stonyhurst College Observatory, the nearest point to the moorlands on the Lancashire side, and have been kindly supplied by the Rev. W. Sidgreaves.

* Read before the British Association (Section B), Glasgow Meeting, 1901.

THE RELATIVE PROGRESS OF THE COAL-TAR INDUSTRY IN ENGLAND AND GERMANY DURING THE PAST FIFTEEN YEARS.*

By ARTHUR C. GREEN, F.I.C., F.C.S., Consulting Chemist and Chemical Engineer.

The coal-tar colour manufacture has well been called the flower of the chemical industries. Although in absolute money value of its products not equalling some other branches of industrial chemistry, it represents the highest development of applied chemical research and chemical engineering, and may well be taken as the pulse of the whole chemical trade. For a country which allows the most scientific branch of chemical industry to languish cannot expect to maintain pre-eminence for long in any simpler branch of chemical manufacture, since the skill trained for attacking the difficult problems of organic chemistry is certain, sooner or later, to be brought to bear on the simpler questions presented in the manufacture of so-called "heavy chemicals" (acids, alkalis, bleach, salts, &c.), and processes hitherto often left to the supervision of foremen will be taken in hand by educated chemists, with consequent improvement in methods of manufacture, better yields, purer products, and cheaper production. The importance of the coal-tar industry cannot, therefore, be estimated alone by the value of its products, for it exerts a widespread effect upon all other branches of chemical manufacture, from many of which it draws its supplies of raw material. As a pregnant example of this influence, which has been especially noticeable during the last decade, I may mention the revolution which is taking place in the manufacture of sulphuric acid, that most important product of the "heavy" chemical trade. A strong demand had arisen in the colour industry for a large and cheap supply of sulphuric anhydride chiefly in connection with the manufacture of alizarine colours and of artificial indigo. With the object of satisfying their own requirements in this respect the Badische Aniline and Soda Works of Ludwigshafen devoted much time and research to the problem of improving the catalytic process usually known by the name of Winkler, a modification of which process had been worked in this country by Squire, Chapman, and Messel since 1876. This endeavour was attended with such success that by means of the process and plant which they finally evolved, they were enabled to produce sulphuric anhydride so cheaply that not only could it be used as such for a large variety of purposes, but, by combination with water, afforded a profitable source of sulphuric acid. This new method of manufacturing sulphuric acid is, for concentrated acid at least, cheaper than the chamber process, and since the product is absolutely free from arsenic and can be produced at any desired concentration, it seems likely to supplant eventually the time-honoured method of manufacture.

Besides exerting a stimulating influence upon the inorganic chemical manufactures, the coal-tar industry has given birth during recent years to several important daughter industries. The manufacture of synthetic medicinal agents, artificial perfumes, sweetening materials, antitoxins, nutritives, and photographic developers are all outgrowths of the

* Read before the British Association (Section B), Glasgow Meeting, 1901.

coal-tar industry, and in great part still remain attached to the colour works where they originated. Of these subsidiary industries the most important is the manufacture of synthetic medicinal preparations, which has already attained to large proportions, and bids fair to revolutionise medical science. The requirements of the coal-tar industry have further led to great advances in the design and production of chemical plant, such as filter-presses, autoclaves, fractionating columns, vacuum-pumps and stills, suction-filters, enamelled iron, aluminium, and stoneware vessels, &c., for the supply of which extensive works have become necessary.

It is a frequently quoted remark of the late Lord Beaconsfield that the chemical trade of a country is a barometer of its prosperity, and the chemical trade of this country has always been regarded as a most important branch of our manufactures. Even those who might be inclined to regard our declining position in the colour industry with more or less indifference would consider the loss of a material portion of our general chemical trade as nothing less than a national calamity. As already pointed out, however, the two are indissolubly connected, the coal-tar industry being an essential and inseparable part of the chemical industry as a whole. It is with the object of ascertaining our present and future prospects in the chemical trade of the world that I propose to compare the relative development of the colour industry in England and Germany during the past fifteen years. It was at the commencement of this period, that is to say in the year 1886, that Professor Meldola in a paper read before the Society of Arts, gave a masterly account of the position of the industry in this country at that date, and sounded a warning note to our manufacturers and business men regarding its future progress. If an excuse is required for my venturing to refer again to a subject upon which so much has been said and written already, it is supplied by the fact that the warnings repeatedly given by those who saw the future clearly (notably by Professor Meldola and Professor Armstrong), have remained largely unheeded. If the conclusions which are forced upon us are unfortunately not of a reassuring nature for our national trade, it is well to remember that nothing is gained by burying our heads in the sand.

The period which we have to consider has been one of extraordinary activity and remarkable development in the coal-tar industry, and before I pass to the economic aspect of the question I will ask you to consider very superficially some of the main points in this advance. In no other industry have such extraordinarily rapid changes and gigantic developments taken place in so short a period—developments in which the scientific elucidation of abstract problems has gone hand in hand with inventive capacity, manufacturing skill, and commercial enterprise. In no other industry has the close and intimate interrelation of science and practice been more clearly demonstrated.

Born in 1858 the colour industry had already attained to a considerable state of development by the year 1886. The period prior to this might well be called the "rosaniline period," since it is chiefly marked by the discovery and development of colouring matters of the rosaniline or triphenylmethane group, such as magenta, aniline blue, Hofmann violet, methyl violet, acid magenta, acid violets, phosphine, Victoria blues, auramine, malachite green, and acid greens. Individual members of other groups had already been discovered, but the latter had not yet attained to the importance which they were destined later to occupy. This is especially the case with the class of colouring matters containing the double-nitrogen radical known as "azo" colours. This group of compounds has, during the fifteen years which we have to consider, attained to such enormous dimensions and importance that this interval may fairly be termed the "azo period." The number of individual compounds belonging to this class which have either been prepared, or are at present preparable, runs into many millions and far exceeds the members of all other groups of colouring matters put together. In commercial importance also they occupy a position at present far in advance of any other group; the employment of some of them (*e.g.*, the azo blacks), amounting to many thousands of tons annually. A great stimulus to the investigation of the azo compounds was given by the discovery by Böttiger in 1884 of the first colour possessing a direct affinity for cotton (Congo-red), which was followed within a few years by a rapidly increasing series of colours of all shades having similar dyeing properties. The azo colours known prior to this time were either basic colours (aniline yellow, chrysoidine, Bismarck brown, &c.), or acid wool colours (xylidine scarlet, croceine scarlet, &c.). The great simplification of cotton dyeing, brought about by the introduction of the new group of azo colours—"benzo" or "diamine" colours as they were called—led to a rapid increase of their number, and compounds containing two, three, four, or more double-nitrogen groups linking together the residues of various paradiamines (benzidine, tolidine, dianisidine, azoxytoluidine, paraphenylenediamine, naphthylenediamine, &c.), to various naphthol-, amidonaphthol-, and naphthylamine sulphonic acids made their appearance in quick succession. Simultaneously therewith proceeded the discovery and investigation of the various isomeric derivatives of naphthalene required as raw products for the preparation of these colours, an investigation which was largely aided by the classical research on the isomerism of naphthalene compounds carried out in this country by Armstrong and Wynne.

Another method of applying azo colours to cotton, by which much faster shades are obtained, was introduced by Messrs. Read Holiday, of Huddersfield, in 1880, and consisted in producing unsulphonated azo compounds on the fibre by direct combination. Owing to the technical difficulties which were at first encountered in applying this process it has only reached its full development during the last few years at other hands than those of its discoverers. The most important colour produced by this method is paranitraniline red, for which over two hundred tons of chemically pure paranitraniline are manufactured annually.

The search for direct cotton colours led the author in 1887 to the discovery of primuline. This compound having a direct affinity for cotton, and containing at the same time a diazotisable amido group, could be used for the synthesis of various azo colours on the fibre which were remarkable for great fastness to washing. It has had a large employment for the production of fast reds, and the new principle of dyeing which it introduced has been considerably extended in other so-called "diazo" colours. The closer investigation of the thiazol group, to which primuline belongs, further led to the discovery of many other cotton colours belonging to this family, amongst the most important of which are the brilliant greenish-yellow called "turmerine" or "Clayton yellow," the light-fast "chlorophenine" or "chloramine yellow," the pure greenish basic yellow "thioflavine," and the fast cotton-pink "erica."

Passing over the stilbene azo colours and the basic azo ammonium or "Janus" colours, there remains a class of azo compounds to which I must shortly refer, namely, the mordant azo colours, which, with the growing demand for faster shades, have recently come into much prominence. In these compounds the presence of an ortho hydroxyl or carboxyl group gives to the colour the property of combining with metallic mordants, especially chromium oxide, and producing therewith insoluble and fast lakes on the wool or cotton fibre.

We now come to the consideration of three analogously constituted groups of colouring matters, namely, the azines, oxazines, and thiazines. The laborious scientific investigations of Fischer and Hepp, Bernthsen, Kehrmann, and others, on the constitution of these groups of compounds, the first members of which (methylene blue, saffranine, and Meldola's blue) were discovered in a very early stage of the industry, when little or nothing was

known of their structure, combined with the theoretical views on the quinonoid structure of such colouring matters promulgated by Armstrong, and adopted by Nietzki, has led to the discovery of many valuable new members of these classes. Amongst the latter may be specially mentioned the rosindulines, indoine blue, induline scarlet, rhodulines, &c.

Passing to the pyrone and acridine groups, in which much investigation has also been conducted, the most notable advances have been the discovery of the "rhodamines," a class of pure basic reds, and of the basic yellows and oranges allied to phosphine.

It is in the alizarine group that next to the azo group the greatest progress must be recorded. The demand for fast colours for calico printing and for dyeing chrome-mordanted wool to withstand severe "milling" operations has led to a long series of investigations and patents for producing new derivatives of anthraquinone. These new products, known in commerce as "alizarine Bordeaux," "alizarine cyanines," "anthracene blues," "alizarine viridine," "alizarine saphirol," &c., are polyoxy- or amidooxy-anthraquinones, for the preparation of which either alizarine or nitroanthraquinones are the usual starting points.

Passing over some smaller groups, we now come to a very peculiar class of dye-stuffs containing sulphur, which, although discovered by Croissant and Brettonière, in 1873, remained confined to a single representative, "Cachou de Laval," until Raymond Vidal, in 1893, obtained a very fast black colouring matter, which dyed unmordanted cotton, by heating para-amidophenol with sulphur and sodium sulphide. The possibility of replacing aniline black in cotton dyeing by a direct colouring matter, and possibly also of obtaining other shades which, though dyed in a single bath, would resist subsequent "cross dyeing" of the wool in mixed fabrics, lent an immense impulse to the study of this class of colouring matters, and although their molecular structure still remains wrapped in obscurity many new representatives have followed each other in rapid succession, ranging in shade from blacks of various hues to browns, olives, greens, and blues. As the most important of these I may mention "Vidal black," "immedial black," "katechine black," "immedial blues," "katechine brown," "katechine green," &c.

It may fairly be claimed, however, that the greatest triumph of the coal-tar industry for the past fifteen years has been the successful production of artificial indigo on a large manufacturing scale.

Returning now from the scientific to the economic aspect of the subject, I will ask you to consider what share we have obtained in the great expansion of trade resulting from all these new discoveries, of which many have originated in this country. The development of the industry in Germany is well illustrated by the following figures:—

Exports from Germany to the World.

	1885.	1895.	1899
	Tons.	Tons.	Tons.
Aniline oil and salt	1,713	7,135	—
Coal-tar colours (excl. alizarine) .	4,646	15,789	17,639
Alizarine colours	4,284	8,927	—

Again, if we take values, we find that total exports of coal-tar colours from Germany amounted in 1894 to £2,600,000, and in 1898 to £3,500,000, an increase of nearly a million in four years. The latter figure is practically the same as that given by Perkin as an estimate of the *world's* total *production* in 1885, showing how great the increase has been since this date.

The value of Germany's *entire* production is somewhat difficult to arrive at. Witt in his report on the German chemical exhibit at the Paris Exhibition gives as the value of the total chemical industry of Germany for the year 1897 the enormous sum of 46¼ million pounds sterling. Of this sum Lefévre estimates that at least one-tenth may be put down to colouring matters, and another tenth to raw, intermediate, and synthetic products from coal-tar other than colours, and he thus assigns for the total annual value of the coal-tar industry of Germany the sum of 9 to 10 million pounds sterling. With the increase in the production of synthetic indigo it may be taken to-day to considerably exceed this figure.

One may well wonder what becomes of this enormous quantity of coal-tar products. According to the United States Consular reports the 3½ million pounds worth of coal-tar colours exported by Germany in 1898 were consumed as follows:—

The United States took	£750,000 worth
The United Kingdom took	£730,000 ,,
Austria and Hungary took ..	£350,000 ,,
Italy took	£225,000 ,,
China took	£270,000 ,,

whilst the rest of the world took the remainder.

The great increase in production in Germany is further shown by the growth in the capital and number of work-people employed. Thus, according to a report of the Badische Works recently issued, the capital of this company, which was increased in 1889 from £900,000 to £1,050,000, will be further augmented this year by the issue of £750,000 worth of debentures. The number of work-people employed by this company in 1900 was 6485, as against 4800 in 1896, an increase of over 33 per cent in four years. The firm of Leopold Cassella and Co., of Mainkur, near Frankfort, have increased the number of their work-people from 545 in 1890, to 1800 in 1900.

(To be continued).

ON THE EXISTENCE OF A NEW ELEMENT ASSOCIATED WITH THORIUM.*

By CHARLES BASKERVILLE.

(Concluded from p. 181).

III. *Determination of the Atomic Weight of Thorium.*

As this is a preliminary paper a detailed discussion of the various atomic weights accorded thorium by the several workers is beyond its scope, and will be reserved for a subsequent communication. Suffice it to say the compounds made use of, as reported by Clarke (*Smithsonian Institution*, "Constants of Nature," Revised 1897, V., 204), viz., the sulphate, oxalate, acetate, and formate, offer little promise of either concordant or satisfactory results. Brauner and Pavlicek (*Chem. Soc. Proc.*, Lond., 1901, xvii., 63) have recently called attention to a serious source of error in using the anhydrous sulphate. The careful work of Brauner (*Chem. Soc. Trans.*, Lond., 1898, lxxiii., 951), on the heptahydrated thorium tetrammonium oxalate gives good results for that substance, but in atomic weight work it is desirable to have as few factors as possible for consideration. It is a matter for surprise that none of the halogen compounds have ever been used. The tetrachloride was selected for this preliminary work. It may be that the bromide will yield even better results.

Preparation of Thorium Tetrachloride.—Thorium dioxide was prepared from the purest insoluble citrate by intense ignition, ground to an impalpable powder in an agate mortar, and an intimate mixture made with a thick paste composed of corn starch and pure sucrose syrup. Balls 5 to 8 m.m. in diameter were made from this, dried, and baked at 140—150° C. in a platinum milk-pan until thoroughly browned. They were then heated in a closed platinum crucible with a Bunsen burner until thoroughly carbonised. About a dozen of these black pellets were placed in a perfectly clean dry combustion tube. Freshly prepared, pure dry chlorine was passed through the tube, that portion immediately surrounding the balls being

* Presented at the Denver Meeting of the American Chemical Society, August 27, 1901.

heated to dull redness. At first a white vapour formed; some settled upon the tube quite a distance from the heat, and some was swept into the lime absorption tower by the chlorine. In Chydenius's paper (*loc. cit.*) it appears that Berzelius observed this "*weisser dampf*," and he states that it is not finely divided thorium chloride. This is the impurity which was noted above. Then beautiful fern-like crystals, only slightly volatile, began to form immediately over and on the balls. These crystals are the purest compound of thorium ever prepared in this laboratory.* After two hours the heat was removed, and the tube allowed to cool in a current of chlorine, which was subsequently removed by pure dry air free from carbon dioxide.

These absorbed water, and were quite soluble. The white volatile vapour mentioned was even more deliquescent. The fernoid crystals were dissolved in water; the solution made up to 100 c.c. in a standard flask, and aliquot portions measured out by means of a calibrated standard burette, whose outlet was so constricted as to deliver $\frac{1}{10}$ c.c. by drops.

Those portions taken for the determination of thorium were measured directly into weighed platinum crucibles, which were placed in perforations of a porcelain plate over a water-bath and evaporated to dryness. The gelatinous oxychloride was gently heated first with a Bunsen burner, and then ignited to a constant weight with the blast lamp. A beautiful white glistening residue of thorium dioxide was obtained.

For the determination of chlorine, measured quantities were taken, diluted to 75 c.c., acidified with 1 to 2 drops pure nitric acid. Just below the boiling-point the chlorine was precipitated with a weighed quantity of silver nitrate prepared according to Stas. The precipitate was caught in a weighed Gooch crucible, the suction flask being placed in an asphalted box. The crucible and silver chloride were then dried in a dark air-bath at 140—150° C. to a constant weight. The acid washed asbestos from which the matte was made was previously digested in boiling hydrochloric acid, then water, then hot nitric acid, and finally washed with boiling water until not the faintest evidence of the presence of halogens was obtained.

The following are the results obtained:—

	Taken.	Thorium dioxide found.	Per 100 c.c.
A.	25 c.c.	0·0903	0·3612
		Silver chloride found.	Cl per 100 c.c.
	10 c c.	0·0812	0·2007
		Thorium dioxide found.	Per 100 c c.
B.	15 c.c.	0·0542	0·36133
		Silver chloride found.	Cl per 100 c.c.
	15 c.c.	0·1220	0·201056

Calculations.

A. $\frac{XO_2}{Cl_4} = \frac{0·3612}{0·2007}$ ∴ X = 223·2

B. $\frac{XO_2}{Cl_4} = \frac{0·36133}{0·201056}$ ∴ X = 223·3

} Atomic weight of thorium.

It is very interesting here to note that both Hermann's (Clarke's "Constants of Nature, Revised 1897, Part V., 204) and Delafontaine's (*Arch. Sci. Phys. et Nat.*, [2], xviii., 343) results obtained from $2ThSO_4.9H_2O$, and corrected by the observations of Hillebrand (*Bulletin U.S. Geological Survey*, No. 90, 29) to $ThSO_4.4H_2O$, give 223·06 ± 0·3426. On account of the doubt as to the composition the sulphate and the wide divergence in the value obtained (223·23) from the accepted atomic weight of thorium, Clarke correctly threw it out of consideration.

From the preliminary values obtained above, which were not reduced to a vacuum, the results assume importance.

As the tetrachloride is so readily decomposed by water, and a direct comparison between a known amount of the tetrachloride and the oxide obtained therefrom is desirable, a complete analysis of the body was made.

Preparation of Pure Anhydrous Ether.—Ether, which had stood over calcium chloride for a year, was decanted over fresh fused calcium chloride, and allowed to remain a week. It was then distilled and placed over freshly cut sodium, and allowed to stand four days. It was again distilled, and placed over fresh sodium, and left three days until no more bubbles of hydrogen escaped. This process was repeated until fresh sheets of sodium showed no tarnishing, and no hydrogen bubbles were observable. It was finally distilled. In all these operations especial precautions were taken to prevent the absorption of a trace of moisture.

More tetrachloride was prepared, and that part of the tube on each side and just above the pellets placed in a perfectly dry Soxhlet apparatus. At the upper end of the reflux condenser was attached a calcium chloride tube. After the apparatus was in place it was learned that the ground glass connection of the condenser was not air-tight. A selected velvet cork was substituted. When the extraction had continued about six hours it was discovered that an overlooked small defect of the cork had permitted the gradual introduction of about a drop of water, which came from the sweating of the condenser overhead. As this vitiated the experiment, the ether was evaporated, and the whole dissolved in water. During the evaporation a small amount of hydrochloric acid was detected in the vapour. For that reason the experiment must be discarded, but the results are given:—

C. { Thorium dioxide found .. .. 0·1020
{ Chlorine found .. .. 0·05636

whence—

$$\frac{XO_2}{Cl_4} = \frac{0·102}{0·05636} \therefore 224·65 \text{ atomic weight.}^*$$

The pellets, which were covered with excrescences of crystals of the tetrachloride, were repeatedly shaken in a small Erlenmeyer flask with about 10 c.c. of pure dry ether. The ether was filtered directly into a weighed platinum crucible, which was placed in a vacuum desiccator in the bottom of which was pure concentrated sulphuric acid, and above chipped paraffin. The tetrachloride appears to be soluble in about 1000 parts of dry ether. Proper precautions were taken to dry the air used to relieve the vacuum of the desiccator and prevent back rush of moist air from the pump. The crucible was dried at 105° C. for half an-hour in an air-bath already heated, and weighed. The finely crystallised tetrachloride was dissolved in 2 c.c. of pure distilled water to decompose the chloride and form the oxychloride, evaporated to dryness, ignited, and weighed. The following results were obtained:—

Tetrachloride used .. .. 0·0822 grm.
Dioxide found .. .. 0·0674 „

hence—

$$\frac{XO_2}{XCl_4} = \frac{0·0574}{0·0822} \therefore 222·13 \text{ atomic weight.}$$

In all calculations O = 16, Cl = 35·45, and Ag = 107·93.

Another ether extract was made as above, weighed, and dissolved in water, and the chlorine determined by titration with a standard silver nitrate solution, using potassium chromate as indicator—method of Pelouze. Tetrachloride used, 0·01 grm.; c.c. of silver nitrate required, 3·9, each c.c. being equivalent to 0·001 grm. chlorine; hence, 0·0039 grm. chlorine or 39 per cent. The percentage of the oxide obtained from the chloride was 69·83.

* I was assisted in the preparation of the tetrachloride and dry ether by Dr. A. S. Wheeler, to whom I wish to express thanks.

* Higher chlorine value decreases atomic weight of thorium.

Calculating for $ThCl_4$:-

	Using 222.	Using 225·5	Found.
Th.. ..	61·03	61·18	
or—			
ThO_2 ..	69·82	70·17	69·83
Cl_4.. ..	38·97	38·84	39·00 per cent

These discrepancies do not deserve discussion, as the data are far too few for ascribing the proper atomic weight to thorium. The last analysis is important, however, as we have secured a substance of known composition, which may be prepared pure, and which lends itself for atomic weight determinations, as the dual constituents, thorium and chlorine, can be estimated with accuracy. The figures hold interest, however, as it may be asserted that the real mass equivalent of thorium is much below that hitherto ascribed to it. It is of greater interest to attribute the old values to a constant unknown impurity in practically all the materials used. This constituent must be an element of much higher atomic weight.

With this evidence of the complexity of thorium the problem now engrossing my personal attention is the separation of the compounds of this element, the proof of their purity and determination of the physical constants and chemical properties. From insufficient data already obtained, in case the element be tetravalent, it appears that the atomic weight lies between 260 and 280. On account of the extensive occurrence in this State (North Carolina) of the monazite sands from which the original material was obtained, if the investigation give a successful issue, I should like to have the element known as *Carolinium*, and have the symbol Cn.

As this is a preliminary paper only, it may not be out of place to state the lines of research bearing immediately upon the subject that are already under way in this laboratory.

1. The preparation of an adequate quantity of perfectly pure thorium compounds with which to continue the study of radio-activity, the spectrum, and to obtain sufficient tetrahalides for the determination of the true atomic weight of that element, which is assuredly different from the number usually accorded it, and dependent at present upon evidence not wholly satisfactory.

2. An investigation of several of the old thorium compounds like the hydrated sulphates, citrates, &c., and determination of their composition.

3. An investigation of the volatile chloride obtained in the preparation of the thorium tetrachloride.

University of North Carolina,
June 1, 1901.

CONTRIBUTIONS TO THE SCIENCE OF THE NITROCELLULOSES.*

By G. LUNGE and J. BEBIE.

(Continued from p. 179).

H. *Influence of Nitration with Higher Percentage of Water on the Stability of Gun-cotton.*

WHILST experimenting upon the influence exerted by different proportions of the nitration acids on the stability of the product, a diminution in the percentage of nitrogen was found to occur upon prolonged boiling of the product with water. In order to test the practical value of the method given for preparation of gun-cotton with such nitration mixtures, which contain 8 to 11 per cent of water, it had yet to be determined whether these products were less stable towards boiling water than those prepared from the quite concentrated acid mixtures. This has so far not appeared probable, but a definite statement on this point is desirable in consideration of its practical significance. For this purpose two nitrations were now carried out: the one (A), with the usual acid mixture of three parts concentrated sulphuric acid and one part fuming nitric acid, *i.e.*, H_2SO_4 69·14, HNO_3 23·91, H_2O 6·07, N_2O_4 0·88; the other (B), with a mixture of the following composition:—H_2SO_4 63·64 per cent, HNO_3 25·54 per cent, H_2O 10·82 per cent.

We will call the nitration products obtained A and B. Both bodies were now treated several times with hot and boiling water, and the influence of this treatment on the percentage of nitrogen determined. The following table gives the results obtained.

Treatment received by the nitration products.	Percentage of nitrogen. A.	Percentage of nitrogen. B.
Washed half-a-day with cold, then one day with hot water.. ..	214·46 c.c. NO 13·45 % N E.P. = 161° t = 3′ 9″	217·58 c.c. NO 13·64 % N E.P. = 153° t = 3′ 5″
Washed half-a-day with cold, then three days with hot water.. ..	215·03 c.c. NO 13·48 % N E.P. = 170° t = 4′ 40″	215·16 c.c. NO 13·49 % N E.P. = 163° t = 4′ 30″
Half-a-day with cold, then one and a-half days with hot water, and finally boiled for two hours, the water showing no acid reaction..	214·78 c.c. NO 13·47 % N	215·33 c.c. NO 13·50 % N
Do. With five hours' further boiling	213·00 c.c. NO 13·36 % N	214·56 c.c. NO 13·45 % N

Product B, therefore, on treatment with hot and boiling water, behaves similarly to A; the nitrogen diminishes slightly, but remains higher than that in A. Accordingly, the nitration with the acid mixtures containing water used by us yields as stable a product as that with the concentrated acid mixtures used formerly.

I. *Behaviour of Different Kinds of Cotton on Nitration, specially with regard to the Preparation of Collodion-Cotton.*

According to Nettlefold, wood-cellulose and cotton behave differently on nitration. With the same acid mixture, he obtained from the former a product with 11·2 per cent N and 41·6 per cent soluble matter; from the latter the highest degree of nitration and a solubility of only 8 per cent. In actual practice, wood-cellulose is not often used for the preparation of collodion-cotton, but it is possible that the difference in the proportion of lignin contained by the various kinds of cotton, as well as morphological differences, might play a certain part.

The view is held in some places that different kinds of cotton show a dissimilar behaviour among themselves, and to this is traceable the phenomenon reported, that, with the same acid mixtures, sometimes soluble and then again only difficultly soluble products are obtained.

With the complicated structure of the cellulose molecule and the numerous possible isomers on the one hand, and the deviating morphological structure of the filaments of different kinds of cotton on the other hand, it must be admitted that this statement is *à priori* possibly accurate.

Researches were now instituted with cottons of different properties for spinning purposes, for which we have to thank Messrs. E. Zollinger-Jenny, in Zürich. The nitration mixture always had the composition 63·84 per cent H_2SO_4, 19·96 per cent HNO_3, 19·2 per cent H_2O; the remaining experimental conditions were naturally exactly the same for all the nitrations.

* *Zeitschrift für Angewandte Chemie*, 1901, Heft 20

Expt.	Sample.	C.c. NO per 1 grm.	N per cent.	Solubility.	Increase.
1.	Chemically pure wadding	187·58	11·76	Completely soluble.	159
2.	American cotton (middling fair).	184·40	11·56		157
3.	American cotton (Florida) . ..	186·21	11·67		153
4.	Egyptian cotton, white (Albassi)	186·39	11·69		155
5.	Egyptian cotton, natural	185·16	11·61		154

Hence, from these five samples no essential difference can be inferred. All the nitration products show complete solubility. The products from the four commercial substances differ in the proportion of nitrogen no more than 0·13 per cent N. This difference is no doubt due to difference in purity of the samples.

Accordingly, we do not think the undesirable deviations and results on nitrating cotton can be explained by the use of different materials as the starting-point, but they are more likely due to unlike conditions of nitration; principally to differences in the proportion of water, which have hitherto been overlooked and considered unimportant.

K. *Examination of Commercial Varieties of Collodion-cotton ("Soluble" Nitrocellulose) for Explosive Gelatin and Art Silk.*

By "collodion-cotton" or "soluble nitrocellulose" is understood products which are used for quite different purposes. In one case, complete solubility in ether-alcohol is of the first importance—to which belongs the material used for surgical and photographic purposes, and, above all, for the Chardonnet art silk. With others, on the other hand, the object is to get a good "explosive gelatin" with nitro-glycerin (in the proportion of 5 to 7 per cent of the nitrocellulose to 95 to 93 per cent nitro-glycerin); this being the foundation of some of the most important explosives. The products which serve best for both purposes are different from one another. Hitherto no definite publication has appeared as to the properties requisite for each case, and the means by which they may be obtained, but for the first purpose (collodion) a smaller proportion of nitrogen than in the second (explosive gelatin) seems requisite.

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING SEPTEMBER 30TH, 1901.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, October 9th, 1901.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 200 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Sept. 1st to Sept. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 200 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall during this month is again below the average; the actual amount measured at Oxford is 1·86 inches, the average for the past thirty-five years is 2·39 inches, showing a deficit of 0·53 inch, which, added to the previous deficit, makes a total of 0·92 inch, or 5·0 per cent on the average.

Our bacteriological examinations of 519 samples have given the results recorded in the following table; we have also examined 44 other samples, from special stand-pipes, wells, &c., making a total of 563 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	215
New River, filtered (mean of 130 samples) ..	7
Thames, unfiltered (mean of 25 samples) ..	873
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 277 samples)..	19
Ditto ditto .. .. highest	141
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 25 samples) ..	266
River Lea, from the East London Company's clear-water wells (mean of 37 samples) ..	17

Of the 444 samples of impounded and filtered water supplied to London and examined bacteriologically during the past month, 32 samples, or 7·4 per cent, were sterile. Not one sample contained as many as 150 microbes, while only eight samples, or 1·8 per cent, contained more than 100 microbes per c.c., thus showing the remarkable purity of the London supply during the past month. The mean number of microbes in the eight excess samples was 118, against a corresponding mean of 212 in six excess samples during August.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

RADIUM.

By W. MARCKWALD.

THE interesting communications of P. and S. Curie, also of Giesel and others, on the production of strongly radio-active bodies from the barium salts arising from pitch-blende, have been hitherto lacking in a more exact description of the method of crystallisation used by the authors. But it may without difficulty be concluded from these publications that radium and barium salts form isomorphous mixtures; for otherwise, on re-crystallisation of a barium chloride containing but little radium salt, pure barium salt would separate from the solution, until the proportion of the salt corresponded to the mixture, but to increase the proportion of radium salt in the mixture by crystallisation would be impossible.

From researches which I carried out with barium chloride from the mixed chlorides, similar in quality to that used by P. and S. Curie as their starting-point, I found this opinion confirmed. Starting with only 100 grms. of this product a strongly active preparation of radium was obtained, and the crystallisation was conducted on the lines of fractional distillation, which is necessary in the case of isomorphous mixtures. For this purpose the salt is left in the water, and allowed to crystallise partially. The first crystallised fraction is richer, relatively, in radium salt than the original material. With continued crystallisation the radio-

activity of the separating product diminishes regularly, until, finally, the salt remaining in solution is scarcely active at all. The first crystallised portion is now dissolved in hot water, separated by crystallisation on cooling from the mother-liquor, which is used for re-crystallising the second portion, and so on. In this way about 90 grms. absolutely inactive barium salt was finally separated off, while the remaining 10 grms. was divided into about 12 fractions of varying degrees of radio-activity.

The best fractions exhibited clearly the interesting properties observed by the above mentioned authors. The anhydrous salt is strongly phosphorescent; the one containing water of crystallisation weakly so, but more strongly radio-active; glass was coloured by it deep brown in a few days. The action upon the barium platinocyanide screen was successfully demonstrated to a large audience, and the action upon the electroscope can be recognised at a distance of 5 d.m.

THE CHEMISTRY OF DEPOSITS IN STEAM BOILERS.*

By W. E. RIDENOUR.

This is is a very old subject, having been worked upon by many eminent chemists on both sides of the Atlantic, and from many different views.

Some have devoted their ideas to the prevention of scale formation inside the boiler, under which heading you will find in literature and on the market at the present time as many remedies as there are patent medicines for the ailments of the human body.

Others have taken up the purification of water outside the boiler; while again, others have debated as to the chemical salts existing in these deposits. With this latter subject I wish to deal, in conjunction with a study of their physical appearance.

Before proceeding with these deposits, I wish to call attention to the vast amount that accumulates in a boiler from a good water for steam purposes in a month's run.

An average of several analyses of a water which is largely used in Philadelphia, the Schuylkill, is as follows (when it is clear):—

	Grains per U.S. gallon.
Organic and volatile	5·060
Calcium sulphate	3·560
Magnesium sulphate	0·602
Sodium chloride	1·167
Calcium carbonate	0·357
Solids	10·746

There are 4·519 grains of scale-forming matter per gallon in this water, which, for a 1000 horse-power plant, the average for these times, and allowing 4 gallons to be evaporated per hour per horse-power, will give the following:—

4 gallons per hour per horse-power.
10 hours per day.

40 gallons per day per horse-power.
26 days per month.

1040 gallons per month per horse-power.
1000 horse-power.

1,040,000 gallons per month per 1000 horse-power.
4·519 grains per gallon of scale-forming matter.
4,699,760 grains.

671 pounds of sediment per month.

* Read before the Chemical Section of the Franklin Institute, March 28, 1901. From the *Journal of the Franklin Institute*, clii., No. 2.

The above are small figures for the average plant, as private wells are generally used, which are much worse, ranging from 25 to 75 grains per gallon; in one case in particular I recall from the soft coal district of this State, it amounted to 83 grains per gallon, and so situated that it had to be used.

Small wonder, then, that so many workers have been attracted to this troublesome subject.

For convenience, I have divided these accumulations into four classes, according to the predominating constituent:—

1. The calcium sulphate scales.
2. The calcium carbonate scales.
3. The silicate scales.
4. The magnesia scales.

The calcium scales are, as a class, very hard and porcelain-like (examples Nos. 7 and 9), but a few are quite soft (example No. 8). They can generally be told from the others with the aid of a simple magnifier, by their glassy or vitreous appearance.

There has been some debate as to how the calcium sulphate exists, whether as a hydrate or an anhydrite.

Prof. V. B. Lewes (Chemical News, 1889, vol. lix., p. 222) states that it is first deposited as a hydrate, $(CaSO_4)_2H_2O$, by coming in contact with the heated plates forms the anhydrite $CaSO_4$. I have always found it to occur as the anhydrite $CaSO_4$ (example No. 7, from South Australia):—

	Per cent.
Moisture at 100° C.	0·23
Calcium sulphate	94·89
Magnesium hydrate	1·98
Silica	0·25
Organic and undetermined	2·65

The calcium carbonate deposits are usually moderately soft, but the presence of even small quantities of either magnesia, calcium sulphate, or silica modifies them to variable degrees of hardness, some equalling those of the first class.

Example of soft scale, No. 10.

Example of hard scale, No. 11.

If moderately pure, they are readily recognised by the magnifier, being composed of distinct crystals (samples Nos. 10 and 15); some being easily seen by the naked eye (samples Nos. 12 and 14). This crystalline appearance is pronounced in some deposits of but 50 per cent calcium carbonate, sample No. 14, which contains—

	Per cent.
Calcium carbonate	51·73
Calcium sulphate	26·10
Magnesium hydrate	11·32
Silica	0·42
Iron oxide and alumina	0·39
Organic and undetermined	10·04

The silicate scales, to me, are the most strange and interesting. They are most common in the Southern States, but I have received a few from different States.

In these scales there is a combination of calcium oxide and silica, existing as calcium silicate, which, I think, is formed during the violent boiling under pressure in the boiler, by the free silicic acid occurring in the water reacting with the calcium carbonate.

Sample No. 2 from Louisiana:—

	Per cent.	Calcium silicate.
Calcium carbonate	36·40	
Calcium oxide	7·32	7·32
Silica	41·00	7·84
Magnesium hydrate	0·50	
Alumina	9·68	15·16
Organic and undetermined	5·10	

Sample No. 3, from New Jersey :—

	Per cent.	Calcium silicate.
Moisture at 100° C.	4·55	
Calcium carbonate	7·47	
Magnesium hydrate	2·74	
Calcium oxide	21·94	21·54
Silica	51·07	23·50
		45·04
Calcium sulphate	1·56	
Iron oxide	1·34	
Organic and undetermined	9·33	

An extreme case is sample No. 4, from Olympia, Washington :—

	Per cent.	Calcium silicate.
Calcium oxide	36·42	36·42
Silica	40·51	39·02
		75·44
Magnesium hydrate	3·04	
Iron oxide and alumina	2·66	
Oil	11·50	
Organic and undetermined	5·87	

Sample No. 16, from this State, is especially interesting, as I was able also to get a sample of the water. The scale contained :—

	Per cent.	Calcium silicate.
Calcium oxide	5·42	5·42
Silica	48·02	5·80
		11·22
Calcium sulphate	3·95	
Magnesium hydrate	3·58	
Iron oxide and alumina	27·08	
Organic and undetermined	11·95	

The water analysed :—

	Grains per U.S. gallon.
Calcium carbonate	1·311
Calcium sulphate	0·104
Magnesium carbonate	1·147
Sodium chloride	0·850
Silica	1·469
Organic and volatile	1·340
Solids	6·221

In comparing these two analyses, it is seen that the calcium carbonate occurring naturally in the water has completely disappeared before forming into scale, making quite possible the hypothesis that the silica has reacted with the calcium carbonate during evaporation.

The silicate scales have no characteristic physical appearance.

The magnesia scales have caused considerable disagreement among the many investigators as to which salt of magnesium is found in these deposits, whether magnesium oxide, magnesium hydrate, or magnesium carbonate. Magnesium hydrate is now the generally accepted combination, and I agree that this is the usual salt occurring.

Sample No. 5, from Texa, contained :—

	Per cent.
Calcium carbonate	4·25
Calcium sulphate	7·50
Magnesium hydrate	82·95
Silica	3·10
Iron oxide and alumina	1·18
Organic and undetermined	1·02

But a few specimens have been examined by me which contained magnesium carbonate.

Sample No. 17, from Pennsylvania :—

	Per cent.
Calcium oxide	4·39
Magnesia	59·79
Carbonic acid	22·29
Silica	5·36
Alumina	2·92
Organic and undetermined	5·25

which is equivalent to—

Calcium carbonate	7·83
Magnesia	38·23
Magnesium carb., $(Mg.CO_3)_4Mg.(OH)_2$	42·25
Silica	5·36
Alumina	2·92
Organic and undetermined	3·41

It is quite possible that magnesium carbonate is first deposited from the water upon being heated, but changes after forming into scale, in proportion to the heat to which it is exposed, into magnesium hydrate, or even magnesium oxide.

There are no marked characteristics under the glass to distinguish these deposits from the others.

It is not safe to express an opinion of a water supply by an analysis of the usual sample of deposit taken from a steam boiler, as exclusive of the influence on the scale of the various preventives used, different portions of the same boiler form scales of quite different composition.

Samples Nos. 12 and 13 are from the same boiler, but are as different as if formed by a carbonate and a sulphate water.

Sample No. 12 contains 96 per cent of calcium carbonate, while No. 13 has 76 per cent of calcium sulphate.

This can be explained if we consider the location in the boiler from which the two samples were taken.

Scale No. 12, composed chiefly of calcium carbonate, came from near the feed-pipe, where the water first comes in contact with the heat, thereby driving off the free carbonic acid and precipitating the calcium carbonate thus held in solution; while the calcium sulphate still remains dissolved until it reaches the hottest part of the boiler, the bottom plate, where sample No. 13 collected. Prof. V. B. Lewes mentions that he examined several scales from different parts of the same boiler, all of which varied considerably.

THE MEASUREMENT OF GOLD AND SILVER BUTTONS IN QUANTITATIVE BLOWPIPE ASSAYS.*

By JOSEPH W. RICHARDS.

(Concluded from p. 183).

Note on the Quantitative Gold or Silver Assay.—The writer makes the fusion on charcoal in preference to a Freiberg carbon crucible, which is often unobtainable. When finished, it is always possible to make the slag quite liquid and then to pour out the lead *in toto*, leaving only clean slag on the charcoal. At first it will be best to pour out on a cold steel anvil or plate, whence the lead may be picked up and placed at once on the cupel for scorifying. The writer has frequently poured the lead directly from the charcoal on the previously heated cupel, and then commenced immediately to scorify, sometimes without even allowing the lead to set. This will usually succeed for one with a steady hand, and several minutes can thus be saved.

In scorifying, if the blowpipe-tip is advanced almost to the nearer edge of the flame, an oxidising flame of great power without a well-defined point is obtained, before which the lead oxidises with great rapidity. 1800 m.grms. of lead were thus scorified to 300 m.grms. in two minutes;

* *Journal of the American Chemical Society*, xxiii., No. 4.

and, in general, one-half to two-thirds of the time usually consumed in scorification can be saved.

For fine cupellation, it is not absolutely necessary to pre-heat the cupel. The button is placed on the freshly-struck cupel, a spot under the button strongly heated, on which the button drops as it melts. Then the cupel is turned slowly, keeping the button half-way up the far side, and the flame always heating the cupel just under it, which is thus dried before the button comes on to it.

By using such devices as the above to save time, the gold or silver assay may often be run through in from ten to fifteen minutes, with an extra five minutes for separately determining gold and silver, if necessary.

Number on the scale.	Weight of gold button.	Weight of silver button.	Volume of the button.
100ths m.m.	M.grm.	M.grm.	Cu. m.m.
2.	0·0001	0·00004	0·000004
3.	0·0003	0·00015	0·000014
4.	0·0006	0·00035	0·000034
5.	0·0013	0·00069	0·000065
6.	0·0022	0·0012	0·00011
7.	0·0035	0·0019	0·00018
8.	0·0052	0·0028	0·00027
9.	0·0074	0·0040	0·00038
10.	0·0101	0·0055	0·00052
11.	0·0134	0·0073	0·00070
12.	0·0174	0·0095	0·00091
13.	0·0222	0·0121	0·00115
14.	0·0277	0·0151	0·00144
15.	0·0340	0·0185	0·00177
16.	0·0413	0·0225	0·00214
17.	0·0495	0·0269	0·00257
18.	0·0588	0·0320	0·00305
19.	0·0692	0·0376	0·00359
20.	0·0807	0·0439	0·00419
21.	0·0934	0·0508	0·00485
22.	0·107	0·0584	0·00558
23.	0·123	0·0667	0·00637
24.	0·139	0·0758	0·00724
25.	0·158	0·0857	0·00818
26.	0·177	0·0963	0·00920
27.	0·199	0·108	0·0103
28.	0·221	0·120	0·0115
29.	0·246	0·134	0·0128
30.	0·272	0·148	0·0141
31.	0·300	0·163	0·0156
32.	0·330	0·180	0·0172
33.	0·362	0·197	0·0188
34.	0·396	0·216	0·0206
35.	0·432	0·235	0·0225
36.	0·470	0·256	0·0244
37.	0·511	0·278	0·0265
38.	0·553	0·301	0·0287
39.	0·598	0·325	0·0311
40.	0·645	0·351	0·0335
41.	0·695	0·378	0·0361
42.	0·747	0·406	0·0388
43.	0·802	0·436	0·0416
44.	0·859	0·467	0·0446
45.	0·919	0·500	0·0477
46.	0·982	0·534	0·0510
47.	1·047	0·569	0·0544
48.	1·115	0·606	0·0579
49.	1·186	0·645	0·0616
50.	1·261	0·686	0·0655
51.	1·338	0·727	0·0695
52.	1·418	0·771	0·0736
53.	1·501	0·816	0·0780
54.	1·588	0·863	0·0824
55.	1·678	0·912	0·0871
56.	1·771	0·963	0·0920
57.	1·867	1·016	0·0970
58.	1·967	1·070	0·1022
59.	2·07	1·126	0·1075
60.	2·18	1·185	0·1131
61.	2·29	1·245	0·1189
62.	2·40	1·307	0·1248
63.	2·52	1·371	0·1309
64.	2·64	1·438	0·1373
65.	2·77	1·506	0·1438
66.	2·90	1·577	0·1505
67.	3·03	1·649	0·1575
68.	3·17	1·724	0·1646
69.	3·31	1·802	0·1720
70.	3·46	1·881	0·1796
71.	3·61	1·963	0·1874
72.	3·76	2·047	0·1954
73.	3·92	2·133	0·2037
74.	4·09	2·222	0·2122
75.	4·25	2·313	0·2209
76.	4·43	2·407	0·2298
77.	4·60	2·504	0·2390
78.	4·78	2·602	0·2485
79.	4·97	2·704	0·2582
80.	5·16	2·81	0·268
81.	5·36	2·91	0·278
82.	5·56	3·02	0·289
83.	5·77	3·14	0·299
84.	5·98	3·25	0·310
85.	6·19	3·37	0·322
86.	6·41	3·49	0·333
87.	6·64	3·61	0·345
88.	6·87	3·74	0·357
89.	7·11	3·87	0·369
90.	7·35	4·00	0·382
91.	7·60	4·13	0·395
92.	7·85	4·27	0·408
93.	8·11	4·41	0·421
94.	8·38	4·55	0·435
95.	8·65	4·70	0·449
96.	8·92	4·85	0·463
97.	9·20	5·00	0·478
98.	9·49	5·16	0·493
99.	9·78	5·32	0·508
100.	10·08	5·48	0·524

Specific Gravity of Gold-silver Alloys.

Silver. Per cent.	Specific gravity.	Silver. Per cent.	Specific gravity.
0	19·258	51	13·488
1	19·099	52	13·409
2	18·940	53	13·331
3	18·785	54	13·254
4	18·632	55	13·178
5	18·483	56	13·103
6	18·335	57	13·029
7	18·190	58	12·955
8	18·047	59	12·882
9	17·906	60	12·811
10	17·767	61	12·739
11	17·631	62	12·669
12	17·497	63	12·600
13	17·364	64	12·531
14	17·234	65	12·463
15	17·106	66	12·395
16	16·979	67	12·329
17	16·855	68	12·263
18	16·731	69	12·198
19	16·610	70	12·133
20	16·491	71	12·069
21	16·374	72	12·007
22	16·258	73	11·944
23	16·144	74	11·882
24	16·031	75	11·821
25	15·920	76	11·761
26	15·810	77	11·700
27	15·702	78	11·641
28	15·595	79	11·582
29	15·490	80	11·525

Silver. Per cent.	Specific gravity.	Silver. Per cent.	Specific gravity.
30	15·386	81	11·467
31	15·283	82	11·410
32	15·183	83	11·353
33	15·083	84	11·297
34	14·984	85	11·242
35	14·887	86	11·187
36	14·791	87	11·133
37	14·697	88	11·079
38	14·603	89	11·026
39	14·511	90	10·973
40	14·420	91	10·921
41	14·330	92	10·871
42	14·241	93	10·819
43	14·153	94	10·768
44	14·066	95	10·718
45	13·980	96	10·668
46	13·896	97	10·619
47	13·813	98	10·570
48	13·730	99	10·521
49	13·648	100	10·473
50	13·568		

ON THE CÆSIUM-ANTIMONIOUS FLUORIDES AND SOME OTHER DOUBLE HALIDES OF ANTIMONY.

By H. L. WELLS and F. J. METZGER.

We have made a thorough study of the double salts formed by cæsium fluoride and antimonious fluoride, with the result that five compounds have been prepared. This is an unusual number for a series of double salts, and it gives a good illustration of the facility with which cæsium forms such compounds.

The salts to be described have the following formulæ :—

Type.	
1 : 3	$CsF \cdot 3SbF_3$
1 : 2	$CsF \cdot 2SbF_3$
4 : 7	$4CsF \cdot 7SbF_3$
1 : 1	$CsF \cdot SbF_3$
2 : 1	$2CsF \cdot SbF_3$

The previously described antimonious double fluorides, all of which were prepared by Flückiger (*Pogg. Ann.*, 1852, lxxxvii., 245), are as follows :—

Type.			
1 : 1	$KF \cdot SbF_3$,		
2 : 1	$2KF \cdot SbF_3$,	$2LiF \cdot SbF_3$,	$2NH_4F \cdot SbF_3$.
3 : 1	$2NaF \cdot SbF_3$,		

The following chlorides, bromides, and iodides have been described :—

Type.

1 : 2 $RbCl \cdot 2SbCl_3$. (Wheeler, *Amer. Journ. Sci.*, [3], xlvi., 269).

3 : 4 $3NH_4I \cdot 4SbI_3 \cdot 9H_2O$. (Schäffer, *Pogg. Ann.*, cix., 611).

1 : 1 $NH_4Cl \cdot SbCl_3$. (Deherain, *C. R.*, lii., 734).
$NH_4I \cdot SbI_3 \cdot 2H_2O$. (Nicklès, *C. R.*, li., 1097).
$KI \cdot SbI_3 \cdot H_2O$. " " "
$RbCl \cdot SbCl_3$. (Remsen and Saunders, *Am. Chem. Journ.*, xiv., 152).

3 : 2 $3KI \cdot 2SbI_3 \cdot 3H_2O$. (Schäffer, *loc. cit.*).
$3NaI \cdot 2SbI_3 \cdot 12H_2O$. " "
$3NH_4I \cdot 2SbI_3 \cdot 3H_2O$. " "
$3RbCl \cdot 2SbCl_3$. (Wheeler, *loc. cit.*).
$3RbBr \cdot 2SbBr_3$. " "
$3RbI \cdot 2SbI_3$. " "
$3CsCl \cdot 2SbCl_3$. (Setterberg, *Öfversigt K. Vetensk. Akad. Förhandl.*, 1882, 23; Remsen and Saunders, *loc. cit.*).

2 : 1 $2NH_4Cl \cdot SbCl_3$. (Deherain, *loc. cit.*).
$2NH_4Cl \cdot SbCl_3 \cdot H_2O$. (Poggiale, *C. R.*, xx., 1180).
$2KCl \cdot SbCl_3$. (Jacquelaine; Poggiale, *loc. cit.*; Benedict, *Proc. Am. Acad.*, xxix., 212).
$2KCl \cdot SbCl_3 \cdot 2H_2O$. (Benedict, *loc. cit.*).

7 : 3* $7RbCl \cdot 3SbCl_3$. (Remsen and Saunders, *loc. cit.*).
$7RbBr \cdot 3SbBr_3$. (Wheeler, *loc. cit.*).
$7KCl \cdot 3SbCl_3$. (Herty, *Am. Chem. Journ.*, xv., 81).
$7KBr \cdot 3SbBr_3 \cdot 8H_2O$. (Herty, *loc. cit.*).

3 : 1 $3NH_4Cl \cdot SbCl_3 \cdot 1\frac{1}{2}H_2O$. (Poggiale, *loc. cit.*).
$[3KCl \cdot SbCl_3]$. (Poggiale, *loc. cit.* It is probable, according to Herty, *loc. cit.*, that $3KCl \cdot SbCl_3$ does not exist).
$3NaCl \cdot SbCl_3$. (Poggiale, *loc. cit.*).

4 : 1 $4NH_4I \cdot SbI_3 \cdot 3H_2O$. (Schäffer, *loc. cit.*).

Upon comparing the cæsium double fluorides with the salts already known, it is to be noticed that two types of the former, 1 : 3 and 4 : 7, do not occur among the latter, and that the 3 : 4, 3 : 2, 7 : 3, 3 : 1, and 4 : 1 types were not found among the cæsium-antimonious fluorides. The absence of a 3 : 2 fluoride is remarkable, since the salt $3CsCl \cdot 2SbCl_3$ is very sparingly soluble, and because this is a very prominent type among the chlorides, bromides, and iodides. It is evident that a close relation does not exist between the cæsium-antimonious fluorides and the other antimonious double halides, and that the types of the former could not have been predicted from a consideration of the latter. In range, the cæsium double fluorides extend farther at the antimony end than the others, while they do not extend as far at the alkali-metal end of the series of types.

When all the types of antimonious double halides are considered, they are remarkable for their large number, ten. This number is probably greater than is the case with any other negative element. The types, 1 : 3, 1 : 2, 4 : 7, 3 : 4, 1 : 1, 3 : 2, 2 : 1, 7 : 3, 3 : 1, and 4 : 1, with two or three exceptions, are the simplest that can exist in such number between the two extremes, and arithmetically they extend almost as far in one direction as the other.

Method of Preparation.—Solutions of cæsium fluoride and antimonious fluoride were prepared by treating cæsium carbonate and antimonious oxide, each with an excess of pure hydrofluoric acid. To the antimonious solution the cæsium salt was gradually added in small quantities, and after each addition the liquid was evaporated and cooled until crystallisation took place. If a homogeneous product was obtained a portion was removed for analysis, and the process was continued until finally the liquid contained a very large excess of cæsium fluoride. In every case the products were carefully inspected to make sure that they were not mixtures, and at least two crops of a salt were always prepared under somewhat different conditions, and were shown by analysis to be identical in composition before they were accepted as true compounds.

Method of Analysis.—The crystals were carefully dried by pressing between filter-papers, and the portions to be analysed were preserved in glass weighing tubes which were coated within with a very thin layer of paraffin. For the determination of antimony and cæsium a portion was heated in a platinum crucible with concentrated sulphuric acid until all the hydrofluoric acid was removed, the residue was dissolved in hydrochloric acid, antimony was precipitated as sulphide, collected on a Gooch crucible, and weighed after drying in a small oven containing carbon dioxide. Cæsium was weighed as normal sulphate. Fluorine was determined by converting it into silicon fluoride, collecting the latter in water, and titrating with sodium hydroxide, according to a modification of Offermann's method. The results of these fluorine determinations were invariably somewhat too low, as we found by testing the method with pure potassium silicon fluoride; hence, the chief value of these deter-

* This type was described as 23 : 10; see Wells and Foote (*Amer. Journ. Sci.*, iii., 461).

minations consists in showing that the salts under investigation were not oxy-compounds.

1 : 2 *Cæsium-Antimonious Fluoride*, $CsF{\cdot}2SbF_3$.—This salt was obtained in the form of beautiful, transparent needles by adding 2 or 3 grms. of cæsium fluoride to a solution of about 50 grms. of antimonious fluoride in somewhat dilute hydrofluoric acid solution, heating to boiling, and cooling. Two separate crops gave the following results upon analysis :—

	Calculated for $CsSb_2F_7$.	Found. I.	II.
Cæsium	26·28	26·44	—
Antimony	47·43	47·36	47·42
Fluorine	26·28	25·23	—

1 : 3 *Cæsium-Antimonious Fluoride*, $CsF{\cdot}3SbF_3$.—This salt crystallises in the form of stout, transparent prisms. It was obtained by evaporating the mother-liquors from the preceding compound, and cooling, or by the use of somewhat less cæsium fluoride in proportion to the antimonious fluoride in a more concentrated solution. Two crops gave the following results :—

	Calculated for $CsSb_3F_{10}$.	Found. I.	II.
Cæsium	19·47	17·81	17·60
Antimony	52·71	52·95	53·89
Fluorine	27·82	27·01	26·84

The rather wide variation of the results from the calculated quantities is probably due to the fact that the crystals were taken from a very concentrated antimonious fluoride solution, and were consequently not quite pure, even after careful drying on paper.

4 : 7 *Cæsium-Antimonious Fluoride*, $4CsF{\cdot}7SbF_3$.—This salt crystallises in transparent plates, and is formed in the presence of a little larger proportion of cæsium fluoride than the preceding compounds. It was obtained, for instance, upon adding about 4 grms. of cæsium fluoride to a mother-liquor from the last salt, and crystallising by cooling. Two crops gave the following results :—

	Calculated for $Cs_4Sb_7F_{25}$.	Found. I.	II.
Cæsium	28·80	28·99	—
Antimony	45·47	46·02	46·03
Fluorine	25·73	24·58	24·61

We cannot say that we are absolutely sure about the formula of this apparently complicated double salt. It cannot be a 1 : 2 compound, for not only is it entirely distinct in appearance from $CsF{\cdot}2SbF_3$, but coming as it does from a strong antimony solution, the results would naturally come too high rather than too low for antimony. The results vary too widely from a 2 : 3 ratio to make that probable, but they approach somewhat more closely the 3 :5 ratio. The following calculations will show that we have selected the most probable formula :—

Calculated for $Cs_4Sb_8F_{31}$.	Calculated for $Cs_3Sb_5F_{19}$.	Calculated for $CsSb_2F_7$.
31·86	29·75	26·28
43·11	44·75	47·43
25·03	25·50	26·28

1 : 1 *Cæsium-Antimonious Fluoride*, $CsF{\cdot}SbF_3$.—In the presence of still greater proportions of cæsium fluoride this salt is produced by cooling the properly concentrated solution. It forms square prisms, the ends of which are not usually modified by any planes. Three crops gave the following analysis :—

	Calculated for $CsSbF_4$.	Found. I.	II.	III.
Cæsium ..	40·43	41·44	41·19	—
Antimony ..	36·47	35·85	35·66	35·52
Fluorine ..	23·10	22·30	—	—

2 : 1 *Cæsium-Antimonious Fluoride*, $2CsF{\cdot}SbF_3$.—This salt is formed under a wide range of conditions when cæsium fluoride is present in large excess in comparison with the antimonious fluoride. It crystallises in apparently rhombic prisms, which are often somewhat flattened. Four crops, made under very different conditions, gave the following results :—

	Calculated for Cs_2SbF_5	Found. I.	II.	III.	IV.
Cæsium ..	55·30	54·81	—	—	—
Antimony ..	24·95	24·72	24·59	24·92	24·64
Fluorine ..	19·75	19·42	—	—	—

By the use of very concentrated cæsium fluoride solutions with comparatively small amounts of antimonious fluoride, no evidence was obtained of the existence of any double salt containing more cæsium fluoride than the one just described.

Cæsium-Antimonious Iodide, $3CsI{\cdot}2SbI_3$.—It appears that no compound of cæsium iodide with antimonious iodide has been described. The sparingly soluble chloride, $3CsCl{\cdot}2SbCl_3$, is well known, and this was the only double chloride that Remsen and Saunders (*Amer. Chem. Journ.*, xiv., 152) were able to prepare, although four rubidium-antimonious chlorides are known. It is evident that the slight solubility of cæsium-antimonious chloride makes it impossible to prepare concentrated solutions of the component chlorides, and consequently prevents the formation of salts of other types. We have found that an iodide which corresponds in composition to the chloride can be readily prepared. It is sparingly soluble in hydriodic acid solutions, and it exists in two distinct forms, one of which is brick-red, and apparently octahedral in form, while the other is yellow, and occurs in thin hexagonal plates. The octahedral salt was prepared by mixing antimonious iodide and cæsium iodide in rather strong hydriodic acid solutions, while the yellow hexagonal salt was made in much less strongly acid solutions, particularly upon diluting them with water, boiling, and cooling. Two crops of each form were analysed as follows :—

	Calculated for $Cs_3Sb_2I_9$.	Found. Red salt. I.	Red salt. II.	Yellow salt. I.	Yellow salt. II.
Cæsium ..	22·39	23·46	—	22·15	—
Antimony ..	13·47	13·91	13·19	14·36	14·52
Iodine ..	64·14	62·98	—	63·03	—

This was the only double iodide that we were able to obtain.

There is little doubt that a corresponding bromide exists, for we observed, while engaged in work with another object in view, that a yellow precipitate is produced when the bromides of cæsium and trivalent antimony are brought together in solution. Having overlooked the fact that the compound had not been described, we neglected to analyse the product.

Cæsium-Antimonic Halides.—So little is known concerning the double halides of quinquevalent elements that it seemed desirable to study the cæsium-antimonic compounds. Setterberg (*Ofversigt K. Vetensk. Akad. Förhandl.*, 1882, 23) has described a single double chloride, $CsCl{\cdot}SbCl_5$, and we have confirmed his result, but by using widely varying conditions we have been unable to prepare any other compound. Setterberg's salt crystallises in long, colourless, transparent needles. A crop of it gave the following results upon analysis :—

	Calculated for $CsSbCl_6$.	Found.
Cæsium	28·54	29·14
Antimony	25·75	26·43
Chlorine	45·71	43·94

We have extended our investigation to antimonic fluoride and cæsium fluoride, but the results were disappointing from the fact that we were able to prepare but one double salt, while Marignac (*Leibig's Ann.*, cxlv., 237) has described two potassium antimonic fluorides. Either cæsium in this case unexpectedly fails to show as

great a tendency to form double salts as does potassium, or else we have failed to find the proper conditions for producing them.

The salt obtained by us apparently contains hydroxyl, although prepared in strong hydrofluoric acid solutions, and has the formula $CsF{\cdot}SbF_4OH$. It crystallises on cooling warm, rather concentrated solutions in the form of bundles of transparent needles. Two crops gave the following analyses:—

	Calculated for $CsSbF_4OH$.	Found. I.	Found. II.
Cæsium	36·44	37·77	—
Antimony	32·87	31·82	31·72
Fluorine	26·03	25·54	26·18
Hydroxyl	4·66	[4·87]	—

—*American Journal of Science*, vol. xi., No. 66.

NOTICES OF BOOKS.

The Periodic Classification and the Problem of Chemical Evolution. By George Rudorf, B.Sc., University College, London. London and New York: Whittaker and Co. 1900.

In attempting to condense a *résumé* of the above subjects into a small text-book of a couple of hundred pages, the author has set himself an important and difficult task. The necessity for such condensation unfortunately lies at the door of our present examinational system; for it is manifestly impossible for the average student, in addition to his many other duties, so to study the original literature involved in the above subjects as to make himself master of all the speculations and theories that have been advanced.

Provided the book is used as a convenient means of bringing before the notice of students a brief outline of the various theories with a view to more complete studies of the original literature, well and good; but if the book is to be used as a sort of concentrated essence to meet the requirements of the Board of Examiners, the matter assumes a more serious aspect, for then it is necessary that the author himself should be a thorough master of the many researches and speculations he seeks to condense, or otherwise there is a danger that both master and pupil "shall fall into the ditch."

That this is no imaginary danger is seen by a cursory examination. For instance, in Sir Norman Lockyer's notes printed on the first page, he says:—"If you well consider J. J. Thomson's work in connection with the dissociation hypothesis, you will find its importance to be that he negatives the old suggestions which you reproduce."

And in the chapter dealing with the question of rare earths there are some very hasty assertions and serious errors, that point to great haste, if not carelessness, on the part of the author. It is stated, on page 146, that Welsbach succeeded in decomposing didymium by fractionally crystallising the double nitrates of "old didymium" with ammonium nitrate; no mention being made of the part played by lanthanum, upon the presence of which depends the whole success of the method. On page 148, the hypothetical bodies, Z_α, Z_β, and Z_γ, of M. Lecoq de Boisbaudran are referred to as having been distinguished by their spark spectra; while, in point of fact, they have their origin in a different kind of spectra altogether, called by de Boisbaudran "reversion spectra." On the same page we are told that Sir William Crookes has separated old yttria into some bodies that he has named, "and are known as, samarium, mosandrum, yttrium, and yttrium-α." It is scarcely necessary to point out that Sir William Crookes is not responsible for any of the above-named elements; and certainly he has never suggested that they form the component parts of old yttria.

Errors and hasty conclusions of this kind, instilled into the mind of a student at the commencement of his scientific career, cannot fail to do harm, and the subjects will have to be re-learned, re-digested later on.

We are sorry to have to point out these faults, because many things in the book will be found of considerable value to the student. We can only hope that he may be able to separate the good from the bad; and, after all, that is what has to be done in the case of most books. It is well printed and indexed.

MEETINGS FOR THE WEEK.

Friday, 25th.—Physical, 5. "On the Variation with Temperature of the Thermo-electromotive Force and of the Electric Resistance of Nickel, Iron, and Copper, between the Temperatures of −200° and +1050°," by E. P. Harrison. "On Asymmetry of the Zeeman Effect," by G. W. Walker.

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THE CHEMICAL NEWS.

Vol. LXXXIV., No. 2187.

ESTIMATION OF CYANIDE IN THE PRESENCE OF A CHLORIDE.

By FRANK B. GATEHOUSE.

When a solution of $AgNO_3$ is added to a solution of KCN in the presence of KCl no precipitate is formed whilst any KCN remains in solution :—

$$2KCN + AgNO_3 = KCN.AgCN + KNO_3.$$
(soluble)

But as soon as the silver solution has been added in quantity, more than sufficient for the formation of the double cyanide, a precipitate is produced :—

$$KCN.AgCN + AgNO_3 = 2AgCN + KNO_3.$$

One molecule of $AgNO_3$ is therefore required for the first reaction, and an equal amount to form the precipitate of AgCN.

Working on the above facts I have found the following volumetric process for estimating KCN in the presence of KCl or NaCl both expeditious and accurate :—

Measure out a definite amount of the solution containing the cyanide and chloride. Run into it from a burette a decinormal solution of $AgNO_3$, until a permanent turbidity appears. At this stage of the process each c.c. of $AgNO_3$ solution which has been used will correspond to 0·013036 grm. of KCN. Note the reading of the burette, and run into the solution the same volume of silver solution as was required to form the permanent precipitate, and again note the reading. From this point the $AgNO_3$ added is used in precipitating the chloride. Then add a few drops of K_2CrO_4 solution free from chloride, and judging the end of the reaction by the appearance of the dark red silver chromate, estimate the chloride in the usual manner.

Merchant Venturers' Technical College,
Bristol, October 16, 1901.

THE RELATIVE PROGRESS OF THE COAL-TAR INDUSTRY IN ENGLAND AND GERMANY DURING THE PAST FIFTEEN YEARS.*

By ARTHUR C. GREEN, F.I.C., F.C.S.,
Consulting Chemist and Chemical Engineer.

(Concluded from p. 187).

Passing now to England, we find that the imports of coal-tar colours into the country are steadily rising, as is shown by the following figures taken from the Board of Trade returns :—

Imports of Coal-tar Dyestuffs into England during the last Fifteen Years (excluding Indigo).

1886	£509,750	1894	£599,000
1887	542,000	1895	710,000
1888	569,000	1896	739,300
1889	609,200	1897	695,400
1890	594,400	1898	739,000
1891	586,300	1899	708,800
1892	542,200	1900	720,000
1893	504,000		

* Read before the British Association (Section B), Glasgow Meeting, 1901.

Contrasted with this, the exports of coal-tar colours manufactured in England have fallen from £530,000 in 1890 to £366,500 in 1899. Comparing these figures with the rapidly increasing export trade of Germany, it is seen that, whereas formerly the English export trade in artificial colours was about one-quarter that of Germany, it does not now amount to a tenth part. It is therefore apparent that we have had but little share in the great increase which this industry has experienced during the past fifteen years, and that we have not even been able to supply the expansion in our own requirements. In order to ascertain what proportion of our own needs we at present furnish, I am able to lay before you the following interesting figures, which have been kindly supplied me by the Bradford Dyers' Association and the British Cotton and Wool Dyers' Association, who together form a very large proportion of the entire dyeing trade :—

Colouring-matters Used by Bradford Dyers' Association.

English ..	10 per cent	Swiss ..	6 per cent
German ..	80 ,,	French ..	4 ,,

Colouring-matters Used by British Cotton and Wool Dyers' Association.

Aniline colours	English ..	22 per cent
	Foreign ..	78 ,,
Alizarine colours	English ..	1·65 ,,
	Foreign ..	98·35 ,,

The English Sewing Cotton Company have also very kindly supplied me with a detailed analysis of their consumption, from which it appears that out of a total of 60 tons of colouring-matters and other dyeing materials derived from coal-tar only 9 per cent were of English manufacture.

The accompanying table of statistics of the six largest German firms gives a fair picture of the present dimensions of the industry in that country. (See next page).

The joint capital of these six firms amounts to at least 2½ millions; they employ between them about 500 chemists, 350 engineers and other technologists, 1360 business managers, clerks, travellers, &c., and over 18,000 work-people. Compared with such figures as these, the English colour manufacture assumes insignificant proportions. The total capital invested in the coal-tar colour trade in England probably does not exceed £500,000, the total number of chemists employed cannot be more than 30 or 40, and the number of workmen engaged in the manufacture does not amount to over a thousand.

A similar relative proportion is maintained in the number of patents for new colouring-matters and other coal-tar products taken by the English and German firms, as is shown by the following table :—

Comparison of Number of Completed English Patents for Coal-tar Products taken during 1886—1900 by Six Largest English and Six Largest German Firms.

German firms—	
Badische Aniline Works	179
Meister, Lucius, and Brüning	231
Farbfabriken Bayer and Co.	306
Berlin Aniline Co.	119
L. Cassella and Co.	75
Farbwerk Mühlheim Leonhardt and Co.	38
Total of six German firms ..	948
English firms—	
Brook, Simpson, and Spiller	7
Clayton Aniline Co.	21
Levinstein	19
Read Holliday and Co.	28
Claus and Reë	9
W. G. Thompson	2
Total of six English firms ..	86

Position of the Six Largest Colour Works in Germany in the Year 1900.

	Badische Aniline Works.	Meister, Lucius, and Brüning.	Farbenfabriken Bayer and Co.	Berlin Aniline Co.	Cassella and Co.	Farbwerk Mühlheim Leonhardt, and Co.	Total of six firms. About—
Capital..	£1,050,000	£833,000	£882,000	£441,000	Private concern	£157 000	£2,500,000
Number of chemists	148	120	145	55	60		500
Number of engineers, dyers, and other technologists .	75	36	175	31		450	350
Commercial staff	305	211	500	150	170		1360
Work-people	6485	3555	4200	1800	1800		18,260
Dividends (per Cent)—							
1897	24	26	18	12½	Not known	9	
1898	24	26	18	15	,,	3	
1899	24	26	18	15	,,	5	
1900	24	20	18	?	,,	Nil	

Nor does the potential loss which we have sustained by our inability to take advantage of a growing industry represent the sum total of our losses. The new colouring matters, made chifley in Germany, have in many cases been introduced as substitutes for natural products, which were staple articles of English commerce. Madder and cochineal have been replaced by alizarine and azo-scarlets, the employment of many dye-woods has greatly decreased, whilst at the present moment logwood and indigo are seriously threatened. Regarding the indigo question, so much has been written that I do not propose to occupy space in its further discussion, but will only point out that the complete capture of the indigo market by the synthetic product, which would mean a loss to our Indian dependencies of £3,000,000 a year, is regarded by the Badische Company as so absolutely certain, that having already invested nearly a million pounds in the enterprise, they are at present issuing £750,000 of new debenture capital to provide funds to extend their plant for this purpose. In the last annual report of the Company they say:—

"As regards plant indigo, the directors are prepared and determined to meet this competition in all its possible variations in value. Much strange matter has been published in India as to improvements in the cultivation and preparation of natural indigo, but the illusions of the planters and indigo dealers are destined to be dispelled before facts, which although they are not known to them, will make themselves more felt the larger the production of artifical indigo becomes."

Again, besides the loss of material wealth which the neglect of the coal-tar trade has involved to the country, there is yet another aspect of the question which is even of more importance than the commercial one. There can be no question that the growth in Germany of a highly scientific industry of large and far-reaching proportion, has had an enormous effect in encouraging and stimulating scientific culture and scientific research in *all* branches of knowledge. It has reacted with beneficial effect upon the universities, and has tended to promote scientific thought throughout the land. By its demonstration of the practical importance of purely theoretical conceptions it has had a far-reaching effect on the intellectual life of the nation. How much such a scientific revival is wanted in our own country, the social and economic history of the past ten years abundantly testifies. For in the struggle for existence between nations the battle is no longer to the strong in arm, but to those who are strongest in knowledge to turn the resources of nature to best account.

The position with which we are confronted is in truth a lamentable one, and the way out is not so easy to find. In 1886 it could perhaps still be maintained that we held the key to the situation if we chose to make use of it; inasmuch as the principal raw products of the colour manufacture (tar oils, naphthalene, anthracene, soda, ammonia, iron, &c.), were in great measure imported from England. In a speech to the Academy of Sciences of Munich, in 1878, Professor von Bäyer had said:—

"Germany, which in comparison with England and France possesses such great disadvantages in reference to natural resources, has succeeded by means of her intellectual activity in wresting from both countries a source of national wealth. Germany has no longer to pay any tribute to foreign nations, but is now receiving such tribute from them, and the primary source from which this wealth originates has its home, not in Germany, but in England. It is one of the most singular phenonoma in the domain of industrial chemistry that the chief industrial nation, and the most practical people in the world, has been beaten in the endeavour to turn to profitable account the coal-tar which it possesses. We must not, however, rest upon our oars, for we may be sure that England, which at present looks on quietly while we purchase her tar and convert it into colours, selling them to foreign nations at high prices, will unhesitatingly cut off the source of supply as soon as all technical difficulties have been surmounted by the exertions of German manufacturers."

Professor von Bäyer could not believe that the English manufacturer and capitalist would stand by and see an important industry which had had its origin and early development in his own country taken from him without a strong effort to retain it. Yet the initial advantages which our natural resources afforded us have been neglected, and now, in 1901, the conditions are completely changed. The adaptation of condensing plant to the Westphalian coke ovens has rendered Germany, though still a large buyer from England, no longer dependent on English tar and ammonia; by the development of the ammonia-soda process she no longer requires English alkali; whilst all other raw products of the colour industry can now be purchased in the commercial centres of Germany at least as cheaply as in England, and some even at lower prices. Through the shortsightedness, ignorance, and want of enterprise of those with whom rested the care of the colour industry of this country in its earlier days, the opportunity has been allowed to pass for ever. The English capitalist passed over as not sufficiently profitable for his consideration an industry which at present amounts to 9 or 10 millions sterling annually, and from which his German *confrère* now reaps a dividend of nearly 20 per cent. The English manufacturer considered that a knowledge of the benzol market was of far greater importance than a knowledge of the benzol theory, and after the early but brilliant days in the infancy of the industry, when guided by such eminent workers as Hofmann, Perkin, and Nicholson, commercial progress and scientific investigation went hand in hand, but little encouragement was given here to chemical investigators and discoverers. The control of the industry unfortunately soon passed into the hands of men who had no knowledge and absolutely no appreciation of the science upon which their business rested, and concerned only with getting the ultimate amount of present profit, discouraged all scientific investigations as waste of time and money. The chemist who devoted himself to the elucidation of the

chemical constitution of a colouring matter was regarded by them as an unpractical theorist of no value to a manufacturing business. Even when he discovered new colouring matters of commercial value they were so blind to their own interests and so incapable of believing that any practical good could come out of such theoretical work that in many cases they refused to patent or in any way take advantage of the discoveries made by him.

During recent years this attitude has certainly undergone considerable modification, and some attempt has been made to call in the aid of the science so long neglected. Certain firms indeed must be given the credit of endeavouring to pursue a more enlightened policy, but these attempts have always been directed too much in the expectation of realising immediate financial results. The difficulties which must be encountered in an attempt to regain the lost ground are of necessity very great and quite unappreciated by our business men. It seems, in fact, to have been the opinion of the public and of the average financial man that this industry ought to be easily won back by us by the establishment of a few technical schools, the engagement of a dozen chemists, and the investment of a few thousand pounds in new plant, forgetting that the supremacy of our German competitors has been won by years of patient toil, by the work of hundreds of trained chemists, and by the outlay of millions of capital. Who can be surprised, therefore, if such expectations have not been realised, and if in spite of some notable successes the general position of the colour trade in England to-day presents a gloomy aspect. During years of stagnation in this country the German manufacturers have been realising large profits, a portion of which they have employed in consolidating their businesses, writing off the value of their buildings and plant, and setting aside enormous reserves (the reserve of the Badische Company is over a million pounds); they have gathered round them perfectly working organisations comprising enormous staffs of scientifically and practicaliy trained research chemists, factory chemists with highly specialised knowledge, chemical engineers, dyers, and others; their travellers and agents are in every part of the globe; by long manufacturing experience and unremitting endeavour to improve their processes and plant, they have brought the yields and quality of their products to such a state of perfection that even when the manufacture of these products is no longer covered by patents, they are able to produce them at a cost price which is impossible to any one commencing their manufacture. They have hedged themselves about with a perfect stockade of many hundreds of patents; have accumulated in their laboratories thousands of intermediate products ready at any time to be subjected to any new treatment or combination which research or theory may suggest as likely to yield new results. By the complete range of colours which they are able to offer in each group of dye-stuffs, whether basic colours, acid colours for wool, fast colours dyeing on metallic mordants, diazotisable colours, or direct colours for cotton, and by the invaluable aid and assistance which they can give the dyer in his daily work, they are enabled to retain his custom, even if it sometimes happens that a better and a cheaper article is offered him by the home producer.

Where then are we to look for an improvement? Some would find a remedy in the imposition of heavy protective tariffs, but such tariffs in France have not availed to prevent a similar state of things there, and protection in colouring matters might have a very detrimental effect upon the textile industries of the country. Others expect salvation from the extension of technical schools, but laudable as is the aim of these institutions I cannot see how they can effect much until their raw material is of a very different character to what it is at present, and until the public can be completely disabused of the fallacy that a year or two of technical training pumped into an ignorant schoolboy will produce a better works-chemist than a university course of scientific study laid upon the foundation of a good general education. Others again base their hopes for the future upon a reform of the patent laws, and seek to compel all patented processes to be worked in this country. Although I am inclined to believe that a portion of our present troubles have been brought about by a bad patent law, framed mainly from an engineering and not from a chemical point of view, and which seems specially designed to foster foreign trade at our own expense, yet I cannot attribute to this cause a too preponderating influence, and am doubtful whether its removal now would materially improve the position. The remedy for the present state of affairs must of necessity be a slow one, and in my opinion can only be found in a better appreciation of the value of science throughout the length and breadth of the land. Until our Government and public men can be brought to realise the importance of fostering the study of science, and of encouraging all scientific industries, until our schools and universities appreciate the importance of a scientific education, until the rewards for public service in science are made equal to those in other branches of the public service, so long will science continue to be held in insufficient esteem in our country. It is not so much the education of our chemists which is at fault as the scientific education of the public as a whole.

When our capitalists more completely realise the importance of calling in the aid of the best scientific skill available, when our universities and technical schools are able to supply a sufficient number of highly educated chemists equal in knowledge, originality, and resource to those trained in German Universities, when our professors and manufacturers are willing to work together in this and other matters, when our patent laws are rendered just to ourselves, we may confidently hope that our natural engineering skill and practical resource will once more bring us to the front.

THE SOLUBILITY OF PHOSPHATIC MANURES IN SOME ORGANIC ACIDS.

By WALTER F. SUTHERST, Ph.D.

The present-day method of valuing phosphatic manures —that is, the neutral and basic ones—by treating them with a dilute solution of citric acid, or, as recommended by Wagner, an acid solution of ammonium citrate, must naturally leave open the question whether such reagents really represent the dissolving-power of the roots of plants or the acids present in the soil. It was this question which led me to try the action of a few organic acids, viz., acetic, tartaric, and citric, on four typical manures, viz., coprolite (Christmas Island), basic slag, basic superphosphate, and precipitated phosphate.

The samples on analysis were found to contain the following:—

	Per cent P_2O_5.		Per cent $Ca_3(PO_4)_2$.
Coprolite	39·67	equal to	84·29
Basic slag	13·31	,,	29·13
Basic superphosphate ..	13·01	,,	28·38
Precipitated phosphate ..	37·03	,,	80·73

The method was as follows:—One grm. of the manure was placed in a 100 c.c. graduated flask, and, in the case in using citric acid, 1 grm. of the pure crystallised acid added and the solution made up to the mark with distilled water. In using the remaining two acids, an amount equal to 1 grm. of citric acid (in the form of normal solutions) was added, so that the total acidity of each solution used was exactly the same. The acid was allowed to act on the phosphate for twenty-four hours, with frequent agitation; then the liquid was filtered through a dry filter-paper, and in 50 c.c. of the filtrate the phosphoric acid was estimated. The portion measured off for the estimation of the phosphoric acid was first made alkaline with ammonia; then acid with dilute nitric acid; then an excess of ammonium molybdate solution added; the solution heated on the water-bath three hours,

allowed to cool and settle. The precipitate was washed with dilute ammonium nitrate solution, and then dissolved in dilute ammonia, from which solution the phosphoric acid was again precipitated by magnesia mixture in the usual way.

I. With Acetic Acid were dissolved out from—

	Grm. $Mg_2P_2O_7$.		Per cent $Ca_3(PO_4)_2$.
a. Coprolite	gave 0·0400	equal to	10·13
b. Basic slag	,, 0·0442	,,	12·30
c. Basic superphosphate	,, 0·0666	,,	18·53
d. Precipitated phosphate	,, 0·1572	,,	43·72

II. With Tartaric Acid—

a. Coprolite	gave 0·1174	equal to	32·60
b. Basic slag	,, 0·0570	,,	15·85
c. Basic superphosphate	,, 0·1020	,,	28·37
d. Precipitated phosphate	,, 0·2808	,,	78·12

III. With Citric Acid—

a. Coprolite	gave 0·0618	equal to	17·17
b. Basic slag	,, 0·0707	,,	19·67
c. Basic superphosphate	,, 0·0891	,,	24·79
d. Precipitated phosphate	,, 0·2562	,,	71·27

On calculating the ratio of dissolved tricalcic phosphate to the total amount present I get the following figures :—

Manure.	Acetic acid. Per cent.	Tartaric acid. Per cent.	Citric acid. Per cent.
Coprolite	12·01	43·41	20·36
Basic slag	42·22	54·41	67·50
Basic superphosphate ..	65·29	87·38	99·26
Precipitated phosphate .	54·15	96·76	88·28

The large difference in the solubilities of the coprolite and basic slag compared with the basic superphosphate and precipitated phosphate is readily explained by the fact that minerals and bodies exposed to a high temperature or fused are much more difficult to dissolve than the same compound when recently precipitated — an instance which one comes across frequently in the laboratory.

Basic superphosphate, invented by Mr. J. Hughes, really belongs to the class of precipitated phosphates, though from its method of preparation—by adding lime to ordinary superphosphate—the reaction which takes place must be a "dry precipitation."

Though citric acid seems to be now fixed upon as the reagent in testing phosphates, it is not at all a true representative, as may be gathered from the above results, for the most satisfactory results as a general solvent are given by tartaric acid.

The Agricultural College,
Holmes Chapel.

CONTRIBUTIONS TO THE SCIENCE OF THE NITROCELLULOSES.*

By G. LUNGE and J. BEBIE.

(Concluded from p. 190).

We have pointed out already that, by observing certain conditions, products completely soluble in ether-alcohol with up to 13 per cent nitrogen may be obtained, which is a higher percentage than that necessary for explosive gelatin. As regards solubility, the relation of a nitrocellulose to ether-alcohol will not be identical with that to nitro-glycerin as solvent, but there should be an analogy between the two cases.

In order to investigate this question we have examined specimens of collodion cotton used in commerce for both purposes before mentioned, viz., (A) of that used for explosive gelatin, and (B) of that manufactured for art silk in Spreitenbach, near Zürich.

* *Zeitschrift fur Angewandte Chemie*, 1901, Heft 20.

Specimen A yielded, per 1 grm., 196·70 c.c. NO = 12·33 per cent N; solubility in ether-alcohol, 95·49 per cent; explosion-point, 198·5°, after warming for 4′ 46″.

Specimen B gave an explosion-point of 197°, after heating for 4′ 45″; therefore, differing immaterially from specimen A. This is the less important that a specimen of highly nitrated gun-cotton from the army factory in Thun, destined for military porposes, is almost identical as regards explosiveness with the less highly nitrated collodion-cotton, as the following figures show. (The experiments were carried out simultaneously in the same apparatus, and hence under the same conditions):—

Collodion-cotton A. (Brig).	Gun-cotton C. (Thun).
E.P. = 197°	E.P. = 195°
t = 4′ 8″	*t* = 4′ 4″
N = 12·33 per cent	N = 13·25 per cent

In other experiments also, we found a somewhat higher explosion-point for collodion-cotton than for well washed gun-cotton. Badly washed products naturally have too low an explosion-point.

In this case little was to be gathered from the stability test, as is seen by the following :—

Specimen.	Beginning of reaction in Abel test.
C. Gun-cotton (Thun)	15′ 17′
A. Collodion-cotton (Brig) ..	No colouration after two hours
B. Collodion-cotton (Spreitenbach)	20′ 24′

Temperature of the water-bath = 80°.

L. *The Behaviour of Nitrocellusoes in Polarised Light.*

The behaviour of the cotton filaments in polarised light is altered by nitration. Its characteristic iridescence with predominating yellow and brownish-yellow illumination is lost. The nitrated filament still shows feeble double refraction, the highly nitrated have a blue iridescence, while no pronounced colour was to be observed in the others. This gives us an excellent means of qualitative examination for unattacked cellulose.

Attempts have already been made to differentiate the various degrees of nitration according to their behaviour in polarised light. According to Morton-Liebschütz, hexa-nitrocellulose should be recognised by the great brightness of the filaments and their grey colour, the penta-nitrocellulose by their blue, and the tetra-nitrocellulose by their yellow colour.

With regard to hexa- and penta-nitrocellulose, we will leave out the observations made by Lunge and Weintraub, as they coincide with ours. Among the numerous products lying between penta- and hexa-nitrocellulose (C_{12}...) which were examined with this view, a mixture of grey and blue illuminated filaments were certainly observable in polarised light. Those in particular were blue in one certain position, and those perpendicular to them, or nearly so; on turning the platform the filaments formerly grey became blue, and *vice versâ*. The grey colour, therefore, cannot be looked upon as a characteristic of any particular degree of nitration.

We did not observe the violet shade between the highly nitrated celluloses and the group of the collodion-cottons mentioned by Chardonnet. From about 198 c.c. NO downwards most of the products showed a grey light, which passes into a soft yellow tone on blending with the top light, and remaining unchanged in many cases. According to Chardonnet, with 160—180 c.c. NO, the colour of the threads changes from straw-yellow to orange. Our products between 170 and 180 c.c. NO were similar to those mentioned above; nothing definite can be said of those under 160 c.c.; in these the structure was more or less destroyed. As the behaviour in polarised light is not only dependent on the chemical composition, but is also a function of the physical properties, conclusive observations were impossible in these cases.

The observation with the polarisation microscope

serves, therefore, where the structure of the filaments is not destroyed (*i.e.*, with nitration with concentrated acid mixtures) to distinguish unchanged cellulose by the iridescency from the highly nitrated products (from deca-nitrocellulose upwards) by the blue illumination; but further distinctions are not possible, and with more dilute acid mixtures (used for collodion cotton), by which the structure may be lost, the recognition of the unchanged cellulose and of the different degrees of the nitration is not possible.

M. *Coloration of the Nitrocelluloses with Iodine.*

The different behaviour towards iodine and sulphuric acid gives a ready means of distinguishing cellulose amongst nitrocellulose. Cellulose assumes a deep blue colour, while nitrocellulose shows the brown colour of the iodine solution, and, after washing the latter, it becomes again white. But their behaviour is different with iodine solution alone, without previous treatment with sulphuric acid. With the true gun-cottons no lasting colouration was to be observed; on the other hand, with the less highly nitrated celluloses, it appeared that the brown colour remained after washing, and increased as the degree of nitration diminished. But this difference of coloration is not sufficiently pronounced to form a foundation for an accurate determination of the degree of nitration.

SOME ABRIDGMENTS IN CHEMICAL CALCULATIONS.*

By Prof. JOSEPH W. RICHARDS.

In calculating the volumes of gases produced from any weight of solid, liquid, or gaseous substance, a few simple relations render the calculations very direct.

The molecular formula of a gas represents in an equation one volume, relatively, of that gas. The molecular weight represents, likewise, a relative weight. If, now, we call the total relative weights entering into a given reaction kilogrms., then each molecule of gas represented in the equation will represent the volume of molecular weight in kilos. of a gas, which, by Avogadro's law, is the same for all gases. For hydrogen this volume is—

$$\frac{2}{0{\cdot}09} = 22{\cdot}22 \text{ cubic metres,}$$

and this is the volume of molecular weight in kilos. of all gases. We can therefore say that, calling the relative weights entering into an equation kilogrms., each molecule of gas in the equation represents 22·22 cubic metres of that gas.

By similar reasoning and calculation we can affirm the relations between the relative weights considered as grms., pounds, or ounces, and the actual volumes thus represented in litres, cubic feet, or cubic inches. We therefore have the following relations:—

If relative weights be—	Each molecule of gas is—
Kilos.	22·22 cubic metres.
Grms...	22·22 litres.
Pounds	355·9 cubic feet.
Ounces	22·24 cubic feet.

(Volumes being at 0° C. and 760 m.m.).

E.g., in the manufacture of acetylene gas—

Molecules of gas = relative volumes 1

$$CaC_2 + H_2O = C_2H_2 + CaO$$

Relative weights .. .. .. 64 + 18 = 26 + 56

Whence it follows that—

64 kilos. of CaC_2 + 18 kilos. of H_2O produce 22·22 cubic metres of C_2H_2.

64 grms. of CaC_2 + 18 grms. of H_2O produce 22·22 litres of C_2H_2.

64 pounds of CaC_2 + 18 pounds of H_2O produce 355·9 cubic feet of C_2H_2.

64 ounces of CaC_2 + 18 ounces of H_2O produce 22·24 cubic feet of C_2H_2.

The most complicated of chemical equations bear the application of these simple principles in a similar manner.

To calculate quickly from the volume composition of a gas the weight of carbon, hydrogen, or oxygen which it will contain in unit of volume, we need only to apply the following principles:—

Equal volumes of all gases contain equal numbers of molecules; therefore, if a gas molecule of any gas whatever contains one atom of carbon, or of hydrogen, or of oxygen, we can say of such gases that equal volumes of them contain equal numbers of atoms of carbon, hydrogen, or oxygen, as the case may be, and therefore equal weights of each of those elements respectively.

But 1 cubic metre of CO contains 0·54 kilo. of carbon; therefore, that statement is true of 1 cubic metre of any other gas with one atom of carbon in its molecule, such as CO_2, CH_4, &c. Gases with two atoms of carbon in their molecule, as C_2H_6, would contain $2 \times 0{\cdot}54 = 1{\cdot}08$ kilos. of carbon by the same principles, and so on to C_3H_8, &c. Carbonic oxide, CO, also contains 0·72 kilo. of oxygen per cubic metre; whence a similar set of relations for CO_2, &c. Hydrogen gas, H_2, contains 0·09 kilo. of hydrogen per cubic metre, whence it follows that 1 cubic metre of a gas with one atom of hydrogen in its molecule, as HCl, will contain—

$$\frac{0{\cdot}09}{2} = 0{\cdot}045 \text{ kilo.}$$

of hydrogen.

We can therefore state that, for a gas containing in its molecular formula one atom of carbon, hydrogen, or oxygen, the weights of those elements present in a given unit of volumes would be—

	Carbon.	Hydrogen.	Oxygen.
In 1 cubic metre	0·54 kilo.	0·045 kilo.	0·72 kilo.
„ 1 litre	0·54 grm.	0·045 grm.	0·72 grm.
„ 1 cubic foot .	0·54 oz.	0·045 oz.	0·72 oz.
„ 1 „ „ .	0·0337 lb.	0·00281 lb.	0·045 lb.

For a gas with two atoms of carbon, hydrogen, or oxygen in its molecule, the respective weights are twice the above; and so on for any gas, no matter how complicated. For practical calculations, I recommend keeping only the above constants in mind, and simply doubling or trebling the volume of the gas, instead of doubling or tripling the constant.

E.g.: Calculate the weight of carbon, hydrogen, and oxygen present in 1 cubic metre and 1 cubic foot of natural gas of the following composition:—

	Per cent.		(By volume).
CO_2	5·7	=	0·057
C_2H_4	0·9	=	0·009
CO	15·4	=	0·154
H_4	8·3	=	0·083
CH_2	3·8	=	0·038
N_2	65·9	=	0·659
	100·0		1·000

Calculation for Carbon.

CO_2	= 0·057
C_2H_4	0·009 × 2 = 0·018
CO	= 0·154
CH_4	= 0·038

0·267 × 0·54 = 0·1442 kilo. per cubic metre.

0·267 × 0·0337 = 0·0090 pound per cubic foot.

* Read before the Chemical Section of the Franklin Institute, March 23, 1901. From the *Journal of the Franklin Institute*, etc., No. 2.

Calculation for Hydrogen.

C_2H_4 .. .. 0·009 × 4 = 0·036
H_2 .. .. 0·083 × 2 = 0·166
CH_4 .. .. 0·038 × 4 = 0·152

0·354 × 0·045 = 0·01593 kilo. per cubic metre.
0·354 × 0·00281 = 0·0010 pound per cubic foot.

Calculation for Oxygen.

CO_2 .. .. 0·057 × 2 = 0·114
CO .. .. = 0·154

0·268 × 0·72 = 0·1930 kilo. per cubic metre.
0·268 × 0·045 = 0·01206 pound per cubic foot.

These principles save much labour, especially in metal lurgical calculations.

ESTIMATION OF HYDRATE IN THE PRESENCE OF ALKALI CARBONATE.*

By W. E. RIDENOUR.

After reviewing the several methods of estimating caustic alkali in the presence of carbonate, and carbonate in the presence of hydrate, the method proposed by R. T. Thompson appeared to be the best, if accurate.

Mr. Thompson ("Sutton's Volumetric Analysis," fifth edition) weighs off a quantity of the sample to be tested, dissolves in water, and titrates with standard acid, using phenolphthalein, which gives the hydrate and half of the carbonate; then, by adding methyl-orange and continuing the titration, the other half of the carbonate can be found.

To test the above method, a solution of sodium carbonate C.P. was made and titrated, with following results:—

Sodium carbonate solution.	Normal hydrochloric acid.	Indicator.
10 c.c.	9·535	Methyl-orange.
	4·574	Phenolphthalein.
10 c.c.	4·985	Methyl-orange.
	9·149	Phenolphthalein.
20 c.c.	9·971	Methyl-orange.
	Decinormal hydrochloric acid.	
10 c.c.	94·78	Methyl-orange.
	45·026	Phenolphthalein.
10 c.c.	49·858	Methyl-orange.

Standard acid, with the factor 1·6377, was used, the sodium carbonate solution was well diluted, and the end of the burette kept below the surface of the liquid.

The indicators (U.S.P., 1890) were also tested; four drops in 100 c.c. of distilled water responded at once to one drop of normal acid and alkali.

A solution of sodium hydrate, C.P., was then made and tested in the same manner.

Sodium hydrate solution.	Normal hydrochloric acid.	Indicator.
10 c.c.	11·822	Methyl-orange.
10 c.c.	11·565	Phenolphthalein.
	0·257	Methyl-orange.
10 c.c.	11·565	Phenolphthalein.
	Decinormal hydrochloric acid.	
10 c.c.	2 67	Methyl-orange.
	115·444	Phenolphthalein.

* Read before the Chemical Section of the Franklin Institute, March 28, 1901. From the *Journal of the Franklin Institute*, cliii., No. 2.

The above would seem to indicate the presence of carbonate in the hydrate, so barium chloride solution (W. Smith, *Journ. Soc. Chem. Ind.*, i., 85) was added to 100 c.c. of sodium hydrate solution in a flask until it ceased to give a precipitate (produced only a slight cloudiness), water added to make 200 c.c., allowed to settle, and the clear liquor titrated.

Clear sodium hydrate solution.	Decinormal hydrochloric acid.	Indicator.
20 c.c.	2·57	Methyl-orange.
	115·464	Phenolphthalein.

If carbonate was present then it is impossible to eliminate the same by precipitation with barium chloride solution.

Combining sodium carbonate and sodium hydrate solutions in various proportions, the following results by titration were obtained:—

Sodium hydrate solution.	Sodium carbonate solution.	Normal hydrochloric acid.	Indicator.
10 c.c.	10 c.c.	16·088	Phenolphthalein.
		5·191	Methyl-orange.
10 c.c.	10 c.c.	21·2796	Methyl-orange.
10 c.c.	1 c.c.	11·9762	Phenolphthalein.
		0·7196	Methyl-orange.
10 c.c.	3 c.c.	12·9528	Phenolphthalein.
		1·6962	Methyl-orange.
		Decinormal hydrochloric acid.	
1 c.c.	1 c.c.	15·98	Phenolphthalein.
		5·60	Methyl-orange.

Note.—Allowance must be made, in proving these results by the factor 104·5726, for the possible presence of carbonate in the sodium hydrate used.

By comparing the different results, it can be seen that phenolphthalein does not indicate half of the carbonate, either alone or in combination with hydrate, but a definite ratio is observed between the results in the titration of pure sodium carbonate when using methyl-orange alone and using phenolphthalein followed by methyl-orange.

Multiply by 2 the number of cubic centimetres of normal hydrochloric acid necessary to neutralise a definite quantity of pure sodium carbonate indicated by methyl-orange, using phenolphthalein, then methyl-orange, and divide by the number of cubic centimetres of normal hydrochloric acid necessary to neutralise the same quantity of pure sodium carbonate, using methyl-orange only, gives 104·5726, *i.e.*,—

$$\frac{2 \times 4{\cdot}985}{9{\cdot}535} = 104{\cdot}5726.$$

For figures, see Table I.

Therefore, to obtain the number of cubic centimetres of normal acid corresponding to the carbonate present in a mixture of alkaline hydrate and carbonate, multiply by 2 the number of cubic centimetres of normal acid indicated by methyl-orange, using phenolphthalein, then methyl-orange, and divide by the factor 104·5726.

Nitromannite and Nitrocellulose.—Léo Vignon and F. Gerin.—One of the authors has already shown that cellulose, when submitted to several degrees of nitration, in all cases gives nitrated derivatives which energetically reduce a cupro-potassic solution. The authors now undertake the examination of the nitrated derivatives of mannite, and examine to find whether the nitric ethers of this alcohol of relatively simple constitution are susceptible of acquiring reducing properties after nitration. Their researches lead them to the following conclusions:—(*a*) Penta- and hexa-nitromannite energetically reduce cupro-potassic solution; (*b*) this property is not attributable to the formation of mannose; (*c*) nitromannite, treated with ferrous chloride, gives no reduction with mannite. With regard to this property, it does not behave like the nitrocelluloses.—*Comptes Rendus*. cxxxiii., No. 14.

ON A SYSTEM OF INDEXING CHEMICAL LITERATURE; ADOPTED BY THE CLASSIFICATION DIVISION OF THE U.S. PATENT OFFICE.*

By EDWIN A. HILL.

In the following paper I will endeavour to describe the system of indexing or digesting chemical literature and patents, now in use in the Classification Division of the United States Patent Office. This division was organised about a year ago to perfect the existing classification of United States patents. Under our laws, no valid patent can be granted for any new process, composition of matter, or chemical body, described in any printed publication prior to the inventor's discovery thereof, or more than two years prior to the date of his application for such patent; and, among other things, this division is now preparing an index or digest of literature and patents relating to chemical bodies and processes, for the use of the office in making its examinations of pending applications.

The system adopted is in the nature of a reference index rather than a classification, and is one elaborated by myself some five or more years since for another purpose, and on which we have been at work since last summer. I may add that our work was well advanced before my attention was called to the fact that there are great similarities between this system and that of Richter.

Generally speaking, in any comparison of digests or indexes that system may be considered best which, in the simplest, most certain, and most direct manner, puts the inquirer in possession of the desired information.

If chemical bodies each had but one instead of many names, and if, in chemical literature, one never met with bodies as yet unchristened, then undoubtedly, the dictionary plan, pure and simple, in which the names of bodies were alphabetically arranged and the references to literature and patents were collected under their proper titles, would answer every requirement, and would be, in fact, the only proper system to use.

Practically, however, most bodies known to chemists have more than one name, many have several, and the names approved in prior decades are generally not the names in highest repute to-day; nor is it likely that the names now in use will in all, or even in most cases, remain those approved in future years.

Where a chemical compound has several names, were it possible to decide now (which perhaps might be done) which one of them was, on good scientific grounds, the most appropriate in view of present knowledge, and further (which, of course, could not be done), could one be assured that such name would remain the approved name for all future time, such title could, without hesitation, be now adopted as the indexing title, under which all references to literature or patents could be entered, and all other titles and names cross-referenced into it; but, while this might be done now in certain cases, who can guarantee that all the names approved to-day shall retain that approbation as our knowledge of chemical constitution is increased?

Evidently the dictionary plan, unmodified, is not the best, and some better system must be devised not open to these objections.

It would seem that the kind and number of the component atoms of a chemical compound are its most unvarying characteristics, and are subject only to the errors of chemical analysis; and that, therefore, these must form the most stable basis for any general scheme for the indexing or digesting of chemical literature; and this conclusion appears to have been independently reached by others than myself; as, for example, by Richter in his recent and former work, and by Jacobsen and Stelzner, following Richter in the index numbers of *Berichte* for 1898 and 1899. We differ chiefly in the methods by which this principle receives practical application.

The simplest, most certain, and most direct system would be to re-cast the empirical formulæ of the compounds, writing the atoms in the alphabetical order of their chemical symbols, and to then arrange the formulæ on an alphabetical basis. For example, take the bodies $(CH_3)_2C_2H_2(NO_2)_2$, $(CH_3)_2CHNO_2$, $KH_3C_2O_4$, CH_3Cl, $Cu(AsO_2)_2$. Re-writing them as above, and arranging them alphabetically, we have As_2CuO_4, $CClH_3$, CCl_4, $C_2H_3KO_4$, $C_3H_7NO_2$, $C_4H_8N_2O_4$.

It should be noted, however, that the compounds containing C and H, and broadly included in the domain of organic chemistry, constitute so large and important a class that we are fully justified in departing slightly from the alphabetical arrangement of chemical symbols, in order to thereby bring more closely together in the index bodies more or less closely related.

Generally speaking, an attempt to combine a dictionary or digest with a classification will be disastrous. We cannot sit on two stools at once, we will surely fall between them; and too much classification grafted on the dictionary or digest idea will give what is neither a good digest nor a good classification.

Classification, as applied to chemical compounds, should be supplementary to, and independent of, a mere digest or reference index.

In practice, therefore, I have modified the purely alphabetical scheme, and have adopted the following general rule for indexing:—

Reject the water of crystallisation, and re-write the empirical formula in the alphabetical order of the chemical symbols, except that in carbon compounds write C first and H second; follow this re-written formula with the constitutional formula, when given, adding the water of crystallisation, if any, but arrange the titles alphabetically by the re-written formula.

The reason for disregarding water of crystallisation may be illustrated as follows:—The three bodies, Na_2SO_4, or anhydrous sodium sulphate, $Na_2SO_4+10H_2O$, or Glauber's salt, and the heptahydrated salt, $Na_2SO_4+7H_2O$, are in this way all indexed under the same indexing formula Na_2O_4S, and are thereby brought closely together, as they should be, in one place in the digest. If, on the other hand, water of crystallisation was taken into account for indexing purposes, the corresponding indexing formulæ would become Na_2O_4S, $H_{20}Na_2O_{14}S$, and $H_{14}Na_2O_{11}S$ respectively, and these three very closely related bodies would, in consequence, be widely separated in the digest, which result would, we think, be a very undesirable one.

Our index is being prepared on the card catalogue plan. The cards used are the regular Library Bureau standard card, No 33, size 7½ by 12½ c.m., or approximately 3 by 5 inches, without rulings except a single blue horizontal line, ruled ⅜ of an inch below the top edge of the card.

The following is a sample set of cards as actually made out in a given instance, except in size.

One Formula Card:

$C_{12}O_{18}Fe_2O_{12}$ or $(CH_3.CO_2)_6Fe_2$

Ferric Acetate; Acetate of Iron; Klaproth's Iron Tincture; Tinctura Ferri Acetatis; Iron Tincture, Klaproth's.

See "A Treatise on Chemistry." By H. E. Roscoe and C. Schorlemmer, vol. iii., "Organic Chemistry," Part I., page 505.

One Polymer or Multiple Formula Card:

$C_6H_9FeO_6$ Polymer Class 2.

See $C_{12}H_{18}Fe_2O_{12}$ or $(C_6H_9FeO_6)_2$

Ferric Acetate.

* Read before the Washington Section of the American Chemical Society, May 10, 1900. From the *Journal of the American Chemical Society*, xxiii., No. 8.

TWO CLASSIFICATION CARDS:

Acetates

Ferric.

See $C_{12}H_{18}Fe_2O_{12}$ or $(CH_3.CO_2)_6Fe_2$.

Iron

Acetate of.

See $C_{12}H_{18}Fe_2O_{12}$ or $(CH_3.CO_2)_6Fe_2$.

FOUR SUBJECT-MATTER OR TITLE CARDS:

Ferric Acetate

See $C_{12}H_{18}Fe_2O_{12}$.

Klaproth's Iron Tincture

See $C_{12}H_{18}Fe_2O_{12}$.

Iron, Klaproth's Tincture of

See $C_{12}H_{18}Fe_2O_{12}$.

Tinctura Ferri Acetatis

See $C_{12}H_{18}Fe_2O_{12}$.

Considering first the formula card, it will be noted that in the formula the atoms are re-arranged in the alphabetical order of their chemical symbols, except that in carbon compounds C comes first, and H second; and that, had there been water of crystallisation in the formula, it would have been rejected. Then follows the constitutional formula, where the water of crystallisation, if any, would appear. Thus had the body been cupric acetate, the first line of the formula card would have been $C_4H_6CuO_4$ or $Cu(C_2H_3O_2)_2+H_2O$. Then follows under the blue ruling, all the names given for the body in question, and, finally, the reference, by volume and page, to the work indexed.

When a citation is to a patent instead of to a book or other printed work, the reference given will be about like this:—

See U.S. Patent No. 319082 to Fahlberg, dated June 2, 1885.

The arrangement of these cards in the card index is strictly an alphabetical one. Thus, all cards reading C_1 take precedence of C_2, C_2 of C_3, &c. In the series C_1, &c., the order of arrangement would be:—

$CAgNO$; $CAgS$; CAg_2O_3; CBr; $CClHgN$; CCl_2O; CCl_4; $CCuN$; $CHAgO_2$; $CHBr$; $CHCl_2I$; $CHCl_3$; CH_2AgNO_3S; CH_2Cl_2; CH_2S; CH_3AsCl_2; CH_3Br; CH_3ClOP; CH_3F; CH_4; CH_5AsClO; CH_5ClN; $CH_6AlNO_8S_2$; CH_6ClN; C_2H_2; $C_2H_3CaClO_2$; C_2H_4AgNO; C_2H_6As; $C_6H_4AgNO_2$; $C_5H_{12}O$; $C_{10}H_{15}Cl_2P$; $C_{22}H_{18}ClN_4O$; $C_{40}H_{52}N_4O_{12}S_2$; CdO_4S; $ClCu$; ClH_2Hg_2NO; DiN_3O_9; HKO_3S; $KMnO_4$; PCl_3; PCl_5; &c.

The foregoing series will fully illustrate the method of arrangement.

The polymer or multiple formula cards perform the following function:—There are many bodies which analysis shows to be composed of certain elements in certain proportions, but for which theory at present indicates a formula containing two, three, or more times as many atoms. Thus, at one time the formula of ferric chloride was written $FeCl_3$, whereas it is now very often written Fe_2Cl_6, and such doubled and tripled formulæ are very common.

In all cases where, in the formula as written, the exponents of all the atoms have a common divisor, after the doubled, tripled, or other form as found is used for preparing the formula card, the formula is then reduced to its lowest terms by dividing the exponents by their greatest common divisor, and a polymer or multiple formula card, made out in the form shown by the foregoing sample ("Class 2," "Class 3," &c., on the polymer cards, indicates the common divisor). In this way the index is rendered independent of any changes in the formula consequent upon future changes of view with reference to constitutional formulæ and other matters of theory.

A mere reference index or digest should in no way depend upon any theory subject to future changes with advancing knowledge. Classification, on the other hand, must necessarily depend on theory, and must change as knowledge is increased.

These polymer cards are sorted in with the regular formula cards to form part of the formula division of the index or digest. We may illustrate the function of these cards thus:—Suppose ferric chloride had been found in the literature under the formula Fe_2Cl_6, and so indexed, but no polymer card made out, and some one consulted the index under the formula $FeCl_3$; the reference, though in the digest, would not be found, but with the polymer card made out the inquirer by it would be referred to the card Fe_2Cl_6, where the required references would appear. All the remaining cards compose the subject-matter or title index, comprised first of the classification cards, second of the regular subject-matter or title cards, and third of any general topics that it may be thought advisable to include in the alphabetical division of the index.

These cards require but little explanation, except that the general statement should be made that all references to the literature or patents of chemical bodies are intended to be entered on the formula card, and all the other cards are merely used as cross references, referring the inquirer to the formula card for all required information.

Classification, it will be noted, is attempted only to a limited extent now, but will be carried out much more completely hereafter, by a supplementary scheme not yet fully perfected—independent of, though based on, the reference index.

The present scheme, however, it will be observed, does incidentally bring together very many closely related carbon and other compounds, and arranges alphabetically, under such general titles as acids, alcohols, ethers, acetates, chlorides, &c., the specific bodies of the given class.

In practice, to use the digest, if the empirical formula of any compound is known, it must be re-written by the rule already given, and at once is disclosed the definite place in the formula index where the desired references, if digested, will be found entered upon the formula card.

If, on the other hand, one of the various names of the body is given, the subject-matter index is entered alphabetically, and a cross reference obtained to the re-written formula with which the formula index is entered for the required information.

The question arises, as between this system and such a one as that adopted in the *Berichte*, which one of them is the best; that is, the most practical for the intended uses? It may be said generally that the Patent Office needs the index for exactly the same purpose as the scientific or practical chemist; *i.e.*, to obtain references to the literature concerning definite chemical bodies, where either the name or the chemical composition or both is given, so that the system best for the one use is probably also best for the other as well.

We consider our system to be preferable, certainly so at least for the Patent Office, and I may say that it was elaborated and adopted without any knowledge of the work of Richter as followed in the *Berichte* by Jacobsen and Stelzner.

In our system the arrangement of the formulæ is governed by the following general principles in the following order:—

1st. The number of C atoms } in carbon compounds.
2nd. The number of H atoms }
3rd. The alphabetical arrangements of the symbols of the remaining elements (including H in other than carbon compounds).

Practically, in indexing, or in using the digest as an index, the only thing to be remembered is, that in carbon compounds C comes first and H second, and that otherwise the re-arrangement of formulæ and the arrangement of such formulæ in the digest is always alphabetically by

the symbols, instead of by the names of the component elements.

That the *Berichte* system is much more complex will be seen at once. Other things being equal, we deem that system which is simplest to be the best, provided it achieves a result of equal value. The ideal system, we think, produces the best result with the minimum of labour, both mental and physical.

In re-writing the empirical formula by the *Berichte* or Richter system, one must remember the following arbitrary established order of precedence of certain of the chemical symbols; viz., C, H, O, N, Cl, Br, I, F, S, P, and this both in re-writing the formulæ and in entering the table. One must also consider the number of carbon atoms in the compound, the number of different varieties of atoms, and various other things as well.

Thus, for example, in the Richter system, the following are the principles which govern, in the order of their relative importance:—

1st. The number of C atoms.
2nd. The number of different kinds of atoms other than C.
3rd. The arbitrary arrangement of ten of the component elements in the following order; viz., C, H, O, N, Cl, Br, I, F, S, P, all taking precedence over the remaining elements.
4th. The arrangement of all other component elements in the alphabetical order of their chemical symbols.
5th. The arrangement of chlorides, bromides, amides, anilides of carbon acids, acetyl and benzoyl derivatives, oximes, phenylhydrazones, &c., under the formulæ of their corresponding bases.
6th. The arrangement in general, of salts, either under the formulæ of their bases, or of their acids.
7th. The arrangement of salts of quaternary ammonia bases under the formulæ of their corresponding hydroxides.

(To be continued).

CATALYSIS IN CONCENTRATED SOLUTIONS.*

By J. M. CRAFTS.

The study of the catalytic action of acids in very dilute solutions has led to the discovery of a number of simple relations between ionic dissociation, chemical affinity, and electrical conductivity, and the conclusion is universally accepted that the active agent is the hydrogen ion. The ratio of the velocity of the reaction to the concentration of the catalysor is nearly constant in dilute solutions of strong acids, but when ionic dissociation is diminished by increasing concentration, or in the case of weak acids by the presence of bodies which reduce the concentration of hydrogen ions, the ratio of velocity to concentration diminishes; a small acceleration has, however, been observed when certain salts are added to the solutions of strong acids. Most of the subjects for experiments, such as the decomposition of esters, the inversion of sugar, &c., do not admit of the employment of very concentrated acid solutions, because the catalysor would then enter into the reaction, forming by-products.

It seemed interesting to study the hydrolysis of the sulphonic acids by means of chlorhydric acid and other strong acids, because here the reaction is catalytic in the sense that it is induced by the presence of a strong acid which does not enter into the final products, nor does it even form intermediate products in the same evident way as in esterification by sulphuric acid or in the oxidation of sulphurous acid through the medium of nitrous fumes, nor does the degree of concentration of the catalysing agent change the nature of the products, which are only sulphuric acid and hydrocarbon.

The results given below show that the rapidity of the reaction instead of being proportional to the concentration of the catalysor, rises to a thirty-fivefold greater rapidity when 38 per cent chlorhydric acid solution is employed instead of 19 per cent, and a very remarkable result was obtained by adding to a 38 per cent chlorhydric acid solution one-half its weight of zinc chloride, the rapidity of the reaction being then raised more than threefold.

It is thus apparent that increased concentration and other influences which must be supposed to diminish ionic dissociation, promote to a high degree the rapidity of the hydrolytic action, and this fact would point to the inference that the hydrolysis is promoted by $HCl + H_2O$, and not by the hydrogen ions, unless some other predominant and preparatory reaction can be attributed to dehydrating agents like chlorhydric acid, sulphuric acid, and zinc chloride. The study of this hypothesis has been undertaken, but seems to demand an extended series of experiments before an opinion can be formed, and it is desired to give in this preliminary notice a description of experiments which establish a sharp distinction between catalysis in dilute and concentrated solutions. It is possible that the newly observed phenomena may be quite different from catalysis, and may require another name, but the old one has been made to hide so many mysteries that it will serve to cover this one also, until a new theory of the reaction can be founded upon a larger number of experiments.

I will give the results of some 150 measurements in sealed tubes chiefly at 100°, and will leave aside a larger number of experiments which were made by passing steam through sulphuric acid solutions of sulphonic acids at different temperatures.

The work will be interrupted for a few months, and it is desired to reserve the field until the projects, which will be indicated for further experiments along the same line, can be executed and the data obtained for explanation, or at least for correct formulation of this interesting reaction.

Experimental Results.

On heating in sealed tubes at 100°, the metaxylenesulphonic acid (1 : 3 : 4) gives an easily measurable rate of decomposition with chlorhydric acid of concentrations varying between 43 per cent and 13 per cent HCl gas; and the intervals of time which it is necessary to heat in order to decompose 10 per cent of the sulphonic acid, vary between thirty minutes and more than 100 hours, according to the strength of the acid. Benzene and toluenesulphonic acids do not react at this temperature, paraxylenesulphonic acid acts very slowly, and the sulphonic acids of the higher homologues of benzene act too rapidly at 100°, and, moreover, these acids are only partly soluble in strong chlorhydric acid even at 100°. For these reasons the first series of determinations was made with the metaxylenesulphonic acid, $C_8H_9SO_3H + 2H_2O$. The crystals of the acid can be kept for any length of time exposed to the air with only slight hygroscopic changes of weight.

A mode of preparation, which was found much more advantageous than the passage by the barium salt, consists in using directly the solution obtained by heating, during two hours at 100°, 2 parts of common sulphuric acid and 1 part hydrocarbon. The immediate product is added cautiously, to prevent heating, to common chlorhydric acid (containing about 38 per cent HCl) cooled to zero or below. Paratoluenesulphonic acid, the common forms of metaxylene and pseudocumene sulphonic acids, and the sulphonic acids of paraxylene and mesitylene, are nearly insoluble in strong cold chlorhydric acid, and the fine crystalline precipitate can easily be washed with pure cold chlorhydric acid with little loss until entirely free from sulphuric acid. Exposure for two days on a glass plate suffices to remove all traces of chlorhydric acid, and to leave the pure sulphonic acids crystallised with their normal proportions of water of crystallisation. The crystalline powder so obtained can be dissolved in water

* *Journal of the American Chemical Society*, xxiii., No. 4.

and re crystallised without change of weight. Paratoluenesulphonic acid has 1 molecule of water of crystallisation; the other acids named have 2 molecules. Paratoluenesulphonic acid so prepared melts at 102°; metaxylenesulphonic acid (1 : 3 : 4) at 59·8°; paraxylenesulphonic acid melts at 86°; pseudocumenesulphonic acid (1 : 3 : 4 : 5) at 112°.

The Hydrolysis, $C_8H_{10}SO_3 + H_2O = H_2SO_4 + C_8H_{10}$.—In each experiment a weighed quantity of the sulphonic acid was sealed with a weighed quantity of chlorhydric acid, or some other substance or acid as a catalysor, in a glass tube of about 1 c.m. diameter, which had been calibrated with weighed amounts of the hydrocarbons, xylene, cumene, &c.

The determinations were made, after heating a definite period, by measuring the height of the layer of hydrocarbon set free. Certain precautions were taken relative to the solubility of the hydrocarbon in the acid solution both hot and cold, and the time required for the complete separation of the dissolved hydrocarbon on cooling. A few control determinations of the sulphuric acid set free were also made, but in this preliminary notice it is not necessary to enter into the details of these operations, because even considerable errors of measurement and impurity of the sulphonic acids would not disguise the nature of the reaction, which it is designed to show.

A well determined and constant temperature was obtained by using the ebullition of pure substances, water, and benzene, under atmospheric pressure. The tubes were always heated in contact with the liquid bath, and allowance was made for the time (about three minutes) required for a thermometer enclosed in a similar tube to take the temperature of 79° or 99°. If the test is made by plunging the glass tube, containing a thermometer and filled with liquid, in a metal tube heated by boiling water to a constant temperature but only containing air, the transfer of heat through the air layer to the glass tube is so slow that nearly an hour is required for the thermometer to reach 100°,

A. *Experiments with Metaxylenesulphonic Acid and Chlorhydric Acid.*—In the following experiments (Nos. I.—XIII.), the temperature was 99·7—100°. The hours from the commencement of heating, and the corresponding percentages of decomposition are given. The latter was usually determined by measuring the hydrocarbon set free in a tube which had been calibrated at the same place with known weights of the same hydrocarbon. It was usually necessary to wait some hours for the complete separation of the hydrocarbon which had dissolved at a high temperature in the acid liquid, but appeared to be almost completely separated in the cold, so that the readings became constant after intervals of an hour.

I. 10 grms. metaxylenesulphonic acid,—

$$C_6H_3CH_3(1)CH_3(3)SO_3H(4) + 2H_2O,$$

+75 grms. chlorhydric acid (10 per cent HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
16	0·0	136	8·7
32	2·2	156	8·7
64	4·3	172	9·4
104	5·6	212	10·0
120	6·5		

The apparent retardation of the decomposition during the first sixteen hours is probably only due to the solubility in the acid mixture of the first fraction of xylene, about 0·04 grm. If this is the case, about 1 per cent should be added to all the measures. The decomposition with a measurable rate of speed up to about 10 per cent, and from that point a decomposition of only 0·6 per cent in forty hours, seems to indicate the presence of an impurity, possibly $C_6H_3CH_3(1)SO_3H(2)CH_3(3)$, which decomposes more rapidly, while the pure acid, $C_6H_3CH_3(1)CH_3(3)SO_3H(4)$, which remains is not decomposed by 10 per cent chlorhydric acid solution.

II. Ten grms. metaxylenesulphonic acid + 75 grms. chlorhydric acid (13·1 per cent HCl). 0·43 grm. xylene was added before heating in order to saturate the acid liquid; the height of the layer of xylene was noted after shaking, and was subtracted from subsequent readings.

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
16	1·9	136	10·2
32	2·4	152	12·0
48	4·2	172	13·8
64	5·4	188	15·7
88	7·9	204	17·4
104	9·0	222	18·7
120	10·2		

The series was terminated by the breaking of the tube.

III. Ten grms. metaxylenesulphonic acid + 70 grms. chlorhydric acid (19 per cent HCl). No corrections were made for the solubility of xylene in the acid solution in this and in the subsequent experiments.

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	1·0	144	40·5
20	6·4	160	44·6
24	9·0	176	47·8
40	14·7	192	51·1
56	20·0	208	54·8
72	21·7	224	58·1
88	25·7	240	61·0
104	30·7	256	63·8
128	36·4	272	66·3

IV. Ten grms. metaxylenesulphonic acid + 30 grms. chlorhydric acid (10·3 per cent HCl) + 8·75 grms. sulphuric acid.

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	1·0	96	31·8
8	2·5	112	36·2
12	4·0	133	40·8
16	7·0	155	46·3
32	12·6	175	51·9
48	17·6	191	55·4
64	23·1	231	63·9
80	27·7	279	70·4
		327	77·0

V. Ten grms. metaxylenesulphonic acid + 93 grms. chlorhydric acid (19 per cent HCl) + 37·5 grms. zinc chloride.

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	3·0	24	30·9
8	13·4	28	31·1
12	16·0	32	34·8
16	22·0	36	38·8
20	26·0	40	42·3

VI. Twenty grms. metaxylenesulphonic acid + 90 grms. chlorhydric acid (25 per cent HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	3·6	52	55·2
8	10·0	56	58·0
12	16·0	60	60·9
16	20·3	64	64·8
20	27·1	68	67·7
24	32·0	72	69·8
28	35·6	88	77·7
32	39·2	104	84·1
36	44·9	120	86·9
40	46·3	136	90·1
44	48·1	152	91·5
48	52·0		

VII. Ten grms. metaxylenesulphonic acid + 515 grms. chlorhydric acid (25 per cent HCl).

Hours.	Xylene. Per cent.
4	2
16	22
20	29

A large bulb with a narrow neck of very thick glass was used. The calibration of the somewhat conical neck was less exact, and the readings were more uncertain than in a tube.

VIII. Twenty grms. of metaxylenesulphonic acid + 70 grms. chlorhydric acid (31·4 per cent HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	14·2	28	83·1
8	29·7	44	92·0
12	47·6	60	96·1
16	57·9	76	95·6
20	68·3	92	95·9
24	76·9		

IX. Ten grms. metaxylenesulphonic acid + 550 grms. chlorhydric acid (31·4 per cent HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
1	6·3	10	35·2
2	9·4	14	44·8
6	20·9	18	60·0

X. Twenty grms. metaxylenesulphonic acid + 70 grms. chlorhydric acid (38·4 per cent HCl).

Hours.	Xylene. Per cent	Hours.	Xylene. Per cent.
4	34·9	48	91·8
8	67·7	64	93·0
12	83·7	80	94·5
16	88·7		

XI. Ten grms. metaxylenesulphonic acid + 38 grms. chlorhydric acid (38·4 per cent HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
½	0	5½	48·9
1	3	6½	56·5
¾	5·7	7½	60·8
1	8·4	8½	66·6
1½	14·0	9½	70·6
2	18·6	10½	72·1
2½	23·5	11½	74·7
3	28·5	13½	79·7
4	37·2	15½	81·0
4½	41·0	17½	82·0

XII. Ten grms. metaxylenesulphonic acid + 39 grms. chlorhydric acid (43 per cent HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
3	38·2	9	90·7
4	68·6	10	91·0
5	77·2	14	92·8
6	86·0	18	94·2
7	89·5	22	97·3
8	90·4	38	97·7

XIII. Ten grms. metaxylenesulphonic acid + 38 grms. chlorhydric acid (38·4 per cent HCl) + 19 grms. $ZnCl_2$.

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
1	28·1	6	92·2
2	55·0	10	96·4
3	75·9	14	97·5
4	86·1	18	99·8
5	90·3	34	99·4

XIV. Temperature 80·2°. Ten grms. metaxylenesulphonic acid + 36 grms. chlorhydric acid (38·4 per cent HCl) + 18 grms. zinc chloride.

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	6·0	20	49·6
8	15·6	24	57·5
12	27·9	28	65·3
16	38·2	32	72·2

(To be continued).

HISTORY OF VOLUMETRIC ANALYSIS.

Prof. L. L. de Koninck, of Liège, has published in the *Bulletin de l'Association Belge des Chimistes* (vol. xv., Jan.-Février, 1901), a sketch of the origin and growth of volumetric analysis which shows impartial study and bibliographic accuracy.

In the labours of Wenzel and of Richter on the reciprocal relations of bases and acids in producing neutral salts (1777 to 1792), is found the law of definite proportions, which lies at the basis of analysis by volume, yet even the germs of this method are lacking. The earliest publication of a volumetric process was by Descroizilles, in 1795, with the title, "Description et Usage du Berthollimètre," and appeared in the "Journal des Arts et Manufactures," vol. i. (reprinted in pamphlet form, Paris, 1802). The instrument herein described, named after the French chemist Berthollet, was devised to measure the value of chlorine water and of bleaching solutions by means of a solution of indigo of known strength. To Descroizilles then belongs the credit of first replacing weights of reagents by volumes of their solutions, as well as of devising graduated cylinders for measuring the liquids. He also had constructed instruments called *acétimètres* and *millilitrimètres*, differing in their graduation; as an indicator in valuing the acid of vinegar he employed litmus-paper. And he was the first to apply this principie of volumetric determination to commercial analyses, yet he did not adopt the fundamental principle which consists in obtaining the weight of a substance by determining the amount of a corresponding reagent, and which allows the direct preparation, by weighing the reagent, of a liquid of definite value. This general principle was first used by Lampadius; the latter describes in his "Handbuch zur Chemischen Analyse der Mineralkörper" (Freyberg, 1801), the method of determining the amount of soda in a sample of crude, natural soda from Hungary; he added sulphuric acid, drop by drop, to a solution of the substance, until it was neutralised, as shown by curcuma, and he then calculated from the weight of the acid used that he had 98 grains of pure soda. This was published five years before Descroizilles made known his first note on alkalimetry in the *Annales de Chimie*, 1806, vol. lx.

This new method, which Dr. de Koninck calls "*titrage stathmométrique*," was not appreciated at its true value by Pfaff, Berzelius, and contemporary chemists, and it was not until Gay-Lussac's researches that its importance in analytical operations was established. Gay-Lussac, without perceiving the universality of the method, saw the possibility of applying it to several special cases, and became the veritable founder of volumetric processes. In 1824 he used this system in valuation of bleaching-powder, in 1828 in analysing commercial potashes, and in 1832 he made the important application to determining silver. He improved on the empiric methods of Descroizilles, and by the invention of the *burette*, graduated after the metric system, gave the process a truly scientific basis.

The next persons to perfect and extend the method were H. Schwarz, of Breslau (who had worked in the laboratory of Pelouze, one of the pupils of Gay-Lussac), who published in 1850 a treatise devoted to "Titrirmethode," and Friedrich Mohr, whose classic work, dated 1855, has since

passed through seven editions, and has been translated into several languages.

Dr. de Koninck in his admirable essay treats of many other details, and so far as possible establishes priority in several instances. He shows that fourteen years after Thomas Clark, of Aberdeen, had patented his soap-test for the hardness of water, Boutron and Boudet submitted a paper to the French Academy of Sciences on "Hydrotimétrie," and on the recommendation of such eminent men as Dumas, Boussingault, Chevreul, and others, Messrs. Boutron and Boudet received a prize of 2000 francs for their contribution, notwithstanding it was little more than an adaptation of the process of Clark!

De Koninck's paper concludes with a bibliography of 116 titles. H. C. B.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 13, September 23, 1901.

Distribution of Acidity in the Stem, Leaf, and Flower of a Plant.—A. Astruc.—There exist in most vegetables free or combined acids, which are soluble in distilled water and easily estimated by titration with an alkaline solution, in presence of phenolphthalein. The author's researches on the distribution of these acids show (1) that the acidity of leaves, more so than that of stems, is in inverse proportion to their age, the youngest consequently being the most acid; (2) that in the same leaf the maximum acidity is found at and round the growing point; (3) that the acidity of the stem diminishes in proportion to the distance from the summit; (4) that the acidity of the flower decreases as the flower changes from a bud into the fully expanded blossom. From the author's experiments it seems always to be the youngest parts of a plant which are the most acid.

No. 14, September 30, 1901.

Formation of Acids in Vegetables.—M. Berthelot and G. André.—The authors' researches show that, in reality, vegetable liquids tend generally to be acid, but the amount of this acidity in no degree represents the total acid present. By far the greater proportion of acid is present in the state of combination with bases, forming soluble salts with potassium, and either soluble or insoluble salts—according to the acid—with lime. In order to obtain the total acidity of a plant, it is not only necessary to titrate the juices against a standard alkali, but also to estimate the alkali present in the ashes of the plant. The mineral acids are usually present in mere traces. The total acidity can thus be obtained by summation.

Calculation of the Heat of Volatilisation and Heat of Fusion of certain Elements.—M. de Forcrand.—From the general relation $\frac{L+S}{T}=\frac{(l+s)M}{T}=30$, which gives the molecular weight M, when l, s, and T are known, the value of L+S can be calculated if values for T and M are known. This calculation is interesting in certain cases, notably in the case of phosphorus. No determination of L has been made for this element, which prevents a rigorous comparison between the corresponding thermometric constants of phosphorus and nitrogen, for example. The heat of fusion, S, of phosphorus is accurately known, and the molecular weight, M, is admitted to be 124 for P_4 at boiling-point (560° absolute). Applying the above formula, $\frac{(l+s)124}{560}=30$ is obtained; from which $l=130{\cdot}4$ cal. and L=16,176 cal. The same method of calculation may be applied to arsenic, selenium, and carbon; but, in the case of carbon, the calculation becomes very uncertain, on account of the vagueness of the boiling-point.

Formation of an Isatinic Derivative of Albumin.—Julius Gnezda.—In a former paper, the author announced the formation of indolic bodies by means of albumin treated with acids. As albumin, when treated with hypochlorous acid, evolves nitrogen, and as a portion of the nitrogen always remains in combination, it is presumed that, when treating albumin with hypochlorous acid, an indolic body remains. Hypochlorous acid being a feeble acid, it may be assumed that the results of its action on albumin may be applied to various conclusions with regard to the constitution of albumin. The author supposes that the new body formed in this way is a chlorisatine, on account of its following reactions:—With potash, it gives a magnificent reddish violet coloration; and when added to silver nitrate and ammonia, it gives again a red powder. These reactions are characteristic of chlorisatine.

MEETINGS FOR THE WEEK.

Thursday, 31st.—Chemical, 8.30. Frankland Memorial Lecture.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Potassium Metabisulphite.—A correspondent wishes to have the chemical formula and mode of preparing this salt.

SOUTH AUSTRALIAN SCHOOL OF MINES AND INDUSTRIES.

Applications are invited up to October 29th for the position of INSTRUCTOR of CHEMISTRY, METALLURGY, and ASSAYING. Salary, £400. Particulars on application to State Agent of South Australia, 1, Crosby Square, London, E.C.

INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

Incorporated by Royal Charter.

NOTICE IS HEREBY GIVEN that the next EXAMINATIONS of the INSTITUTE of CHEMISTRY, for persons desirous of qualifying themselves to be Public and Technical Analysts, will be held at 30, Bloomsbury Square, London, W.C., in January, 1902.

The Examinations are open only to such candidates as have complied with the regulations.

The Intermediate Examination will occupy at least four days, commencing on Tuesday, January 7th.

Examinations in the following branches of the Final Examination for the Associateship (A.I.C.) will extend over at least four days, and may commence on either January 7th or 14th:—

(*a*) Mineral Chemistry; (*b*) Metallurgical Chemistry; (*c*) Physical Chemistry; (*d*) Organic Chemistry; and (*e*) the Analysis of Food and Drugs, and of Water, including an Examination in Therapeutics, Pharmacology, and Microscopy.

(The Final Examination in the branch of Biological Chemistry is held in October of each year).

Applications for admission to the January Examinations should be forwarded to the Registrar not later than Tuesday, December 3rd, 1901, on which day the list of candidates will be closed.

(By Order of the Council)
30, Bloomsbury Square, London, W.C.
October, 1901.
RICHARD B. PILCHER, Registrar and Secretary.

*** "The Regulations for the Admission of Students, Associates, and Fellows of the Institute of Chemistry" may be obtained from Messrs. Blundell, Taylor, and Co., 173, Upper Thames Street, London, E.C., price One Shilling.

THE CHEMICAL NEWS.

VOL. LXXXIV., No. 2188.

VOLUMETRIC ESTIMATION OF MANGANESE.

By HUGH RAMAGE, B.A., A.R.C.Sc.I.

A PAPER on the above subject, by Jos. Reddrop and the present author, was published in the *Journ. Chem. Soc.* for 1895, p. 268. A nitric acid solution of the sample is prepared, the acid being about 4N, and oxidised in the cold by "sodium bismuthate." After filtration the permanganic acid is reduced by "a slight excess" of hydrogen peroxide, and the excess of this reagent determined by titration with N/10 potassium permanganate. Sulphuric acid may be present during oxidation, &c., and also hydrofluoric acid (Ibbotson and Brearley, CHEM. NEWS, vol., lxxxii., p. 269). The solution must be free from chlorine. The procedure was described for the analysis of ferromanganese, spiegels, wrought-iron, steel, and pig-iron, and also for "ores, &c., of manganese." The method has been successfully applied to the analysis of manganese bronzes.

The experiments by which this method of analysis was perfected were made in the Crewe works laboratory in 1891, and the method has been in constant use since that time. Further experiments were made by the author in the summer vacation of 1894, and after this work the paper was written.

No question of inaccuracy has been raised regarding the results obtained in the analysis of ferromanganese and spiegels, but the results have been questioned in the analysis of steel and iron. It has been found, for instance, that the gravimetric method gave higher results than this method. The original paper, however, explained the cause of this. The work of Hartley and the author* on the spectrographic analysis of iron, iron ores, &c., has proved the fact that traces of nickel, cobalt, copper, lead, metals of the alkaline earths, and alkalis, are frequently present in iron ores, and that part of these metals pass into the iron smelted from them. These metals are wholly or partially precipitated with manganic hydrate in the gravimetric process, for this has been proved by spectrographic analysis. Samples of steel, made from ores containing traces of these metals, were found to contain 0·024 per cent of copper and 0·049 per cent of nickel and cobalt. These quantities would raise the results appreciably.

Ibbotson and Brearley have called attention to the fact that the authors of the original paper (CHEM. NEWS, vol. lxxxii., p. 269), "offer no reason why, for steels and low manganiferous alloys, the hydrogen peroxide is added to the permanganate, and for spiegels and highly manganiferous alloys the permanganate is filtered into the peroxide. The distinction is a necessary one; can it be explained?" The fact that higher results are obtained by the latter procedure has caused doubts to be raised regarding the accuracy of the results obtained by the original method. Experiments have been made to discover the cause of the above differences, and to further test the accuracy of the results obtained by the original method. My friends in the Crewe laboratory have shown great interest in this investigation, and have made many experiments. More recently the author has been free to assist, and, with Mr. Ryder's most able assistance, has completed the work. All the possible sources of error we could think of have been considered.

* *Proc. Roy. Soc.*, vol ix., p. 393; *Journ. Iron and Steel Inst.*, II., 1897; *Engineering*, September, 1897, p. 395; *Trans. Roy. Soc.*, vol. cxcvi., p. 502.

These experiments have established the fact that the original method gives accurate results. The best results are obtained by adding an excess of from 1·5 to 3·0 c.c. of the hydrogen peroxide solution; the difference from the true result does not then exceed 0·01 per cent. Each c.c. of hydrogen peroxide outside these limits causes an error of about 0·01 per cent.

The method which will be found most suitable for steel and iron works is as follows:—

Wrought-iron, Steel, and Pig-iron.

Dissolution of Sample.—Weigh out 1·1 grm. of the sample, and place it in a beaker or boiling-tube; add 30 c.c. of dilute nitric acid (approx. 5N), and boil. If a part remains undissolved, decant the solution, filter off carbonaceous matter if necessary, and add more nitric acid up to 25 c.c. If the sample dissolves completely use the 25 c.c. of acid to wash the tube. The free acid in the solution thus prepared is about 4N. If the sample contains much silicon care must be taken, when boiling, not to unduly concentrate the acid, or the silicic acid will separate in a form which blocks up the filter.

Oxidation and Titration.—Cool the solution in a beaker to about 16°, oxidise with 2 grms. of "sodium bismuthate," stir for three minutes, and filter through an asbestos filter into a clean flask. Add hydrogen peroxide solution (approx. N/10 in N nitric acid), from a burette until the *reddish* colour disappears; then add from 1·5 to 3·0 c.c. in excess, and titrate with N/10 potassium permanganate. The hydrogen peroxide must be standardised by the process described in the original paper.

Each c.c. of hydrogen peroxide (N/10) reduced by the sample = 0·1 per cent of manganese.

The reddish colour mentioned above is produced by a secondary reaction during the titration, probably between the permanganic acid and the reduced manganous nitrate. A small quantity of manganic salt appears to be formed, and the yellow colour of this masks the colour of the permanganic acid. This yellow solution is more difficult to reduce than the solution of permanganic acid, and the tinctorial power of the compound is much less than that of the acid; hence the necessity for adding an excess of hydrogen peroxide. Experiment shows that ferrous sulphate produces a much larger proportion of this yellow compound than hydrogen peroxide does.

With reference to the point raised by Ibbotson and Brearley it may be stated that the authors of the original paper conducted several analyses in both ways, and obtained results in close agreement with one another. The method of titration was recommended because the quantity of manganese in the samples we received varied between the widest limits, and we could not be sure of adding "a slight excess" of hydrogen peroxide to the flask before filtration. It has been discovered in the recent experiments that hydrogen peroxide and ferric nitrate react in some unknown way, and that for each c.c. of the former added to a solution containing 1·1 grm. of steel or iron in nitric acid, about 0·1 c.c. is immediately reduced. This reaction exerts a slight influence on the results obtained by the original method in the analysis of iron and steel, and the instructions to "add a slight excess of hydrogen peroxide" are now given more precisely.

Another small error has been discovered in the original method which tends to correct the foregoing. This error is due to a slight reduction of permanganic acid which takes place during, and after, filtration. In amount it is between 0·01 and 0·015 per cent, and the excess of hydrogen peroxide recommended corrects this. The cause of this reduction is not quite clear, but it may be prevented by more complete oxidation of the solution of the sample. This was effected as follows:—After the sample had dissolved in 30 c.c. of dilute nitric acid, the solution was cooled to about 40°. Half a grm. of sodium bismuthate was then added and the solution heated to boiling, and boiled for three minutes. It was then cooled to the ordinary temperature, and a slight excess of sulphurous

acid added to reduce the precipitated oxide of manganese. After oxidation with 1·5 grm. of "sodium bismuthate," and filtration in the usual way, hydrogen peroxide was added from a burette until the reddish colour disappeared and left a clear yellow coloured solution. An excess of from 0·6 to 1·0 of hydrogen peroxide was then added, and the solution titrated with N/10 potassium permanganate. The end of the reaction was more sharply defined in these experiments than in the ordinary method. It was, with some samples, necessary to add more than 0·5 grm. of sodium bismuthate.

The following test experiments were made by this method. The "Farnley iron" contained 0·013 per cent of manganese, and the test solutions were prepared by adding N/10 potassium permanganate to this iron before adding the nitric acid to dissolve it:—

N/10 potassium permanganate added to 1·1 grms. of Farnley iron.	Hydrogen peroxide solution.	Potassium permanganate required. N/10.	Manganese, per cent.		
			Present.	Found.	Difference.
C.c.	C.c.	C.c.			
2·5	3·0	0·35	0·263	0·259	−0·004
5·0	6·0	0·75	0·513	0·513	0
10·0	10·5	0·15	1·013	1·019	+0·006
15·0	16·0	0·5	1·513	1·518	+0·005

The following are the results obtained by this more refined method, and for comparison those obtained by the original method in ordinary laboratory practice:—

Sample.	Combined carbon. Per cent.	Manganese, per cent.	
		Most accurate method.	Original method.
File steel, No. 17 ..	0·90	0·433	0·44
Sample, No. 66 ..	0·58	0·762	0·76
Sample, No. 163 ..	0·42	1·388	1·41

No further tests of this nature were considered necessary. The method followed in the Crewe laboratory was to add the hydrogen peroxide from a pipette, in 5 c.c. at a time, until the colour was discharged. The excess, therefore, never exceeded 5 c.c.

The accuracy of the method appears now to be beyond question, and as the whole analysis has been completed in twelve minutes by the ordinary method it may be recommended for use in all steel and iron works. Recent work has given prominence to the part played by manganese in soft steels, and a method for the estimation of this metal, which is both accurate and rapid, should prove of great value to the manufacturers and to engineers.

St. John's College, Cambridge.

Congress of Russian Naturalists and Doctors of Medicine.—On January 2nd, 1902 (December 20th, 1901, Old Style), the Eleventh Congress of Russian Naturalists and Doctors of Medicine will be opened at St. Petersburg. The Executive Committee consists of the President, Prof. N. A. Menchoutkine; the Vice-President, Prof. A. A. Inostranzeff; and the Secretaries, Profs. I. I. Borgman and W. T. Chewiakoff. The Congress will be divided into the following Sections:—Mathematics and Mechanics, Astronomy and Geodesy, Physics, Physical Geography, Chemistry, Geology and Mineralogy, Botany, Zoology, Anatomy and Physiology, Geography, with a sub-section on Statistics, Agronomy, Scientific and Hygienic Medicine. The Congress will sit from the 2nd to the 12th January, 1902. General meetings will be held on the 2nd, 8th, and 12th January, and the Sections will meet on the 3rd, 4th, 5th, 6th, 9th, 10th, and 11th of January. All those who wish to take part in the meetings as members of the Congress are invited to send their full addresses, and their subscriptions (three roubles), together with the name of the Section they wish to join, to the Executive Committee of the Congress, at the University of St. Petersburg, before December 15th, 1901.

ON A SYSTEM OF INDEXING CHEMICAL LITERATURE; ADOPTED BY THE CLASSIFICATION DIVISION OF THE U.S. PATENT OFFICE.*

By EDWIN A. HILL.

(Concluded from p. 205).

By way of comparison, I have taken from the pages of the *Berichte* index a number of bodies, with the formulæ written and arranged as there shown, and have re-written and re-arranged them on our own classification division plan.

Formulæ taken from the Berichte Index.

(Pages refer to *Berichte*, No. 19, of 1899).

CO_2, CCl_4, CS_2, CHN } p. 3448.

$CHCl_3$, $CHBr_3$, CH_2O } p. 3449.

C_1: CH_2N_4, CH_2I_2, CH_3N_5, CH_3Br, CH_4O_3, CH_5N } p. 3450.

$COCl_2$, CNBr, CHO_2Cl, CHNS

$CO_4N_2Br_2$, CHO_4N_2Br } p. 3451.

C_2H_2, C_2Cl_6, C_2HN_3 } p. 3452.

$C_2Cl_6Hg_6$, $C_2I_2Hg_2$ } p. 3453.

C_2HOCl_3, $C_2H_2O_8N_4$, $C_2H_2N_3Cl$, $C_2H_3O_2Cl_3$, $C_2H_3O_2Br$ } p. 3454.

C_2: $C_2H_4O_7S_2$, $C_2H_4N_2Cl_2$, $C_2H_5O_2N$, $C_2H_5N_2Cl_3$, $C_2H_6O_3S$, C_2H_6NBr } p. 3455.

$C_2HO_2Cl_3Hg_3$

C_3: C_3H_6, C_3H_6O } p. 3456.

C_3: $C_3HO_2N_5$, C_3H_3OBr, C_3H_3OCl, C_3H_3OBr } p. 3459.

$C_3H_6O_4S$

C_3: $C_3H_6N_2S$ } p. 3460.

C_3H_9ON, C_3H_9NS, $C_3H_{12}ON_2$, $C_3H_5O_2N_3S$, C_3H_6ONBr } p. 3461.

C_4H_4O

C_4: $C_4H_{12}N_2$, $C_4N_2H_4$, $C_4H_2O_4N_2$ } p. 3464.

$C_4H_{13}ON$, $C_4H_7ON_3S$ } p. 3466.

C_5H_{12}, $C_5H_4O_2$

C_5: $C_5H_{11}N$, $C_5H_{14}N_2$, $C_5HN_4Cl_3$ } p. 3470.

$C_5H_2O_3Cl_4$, p. 3471.

$C_5H_{15}O_2N$

$C_5H_2ON_4Cl_2$

C_6H_6, C_6H_4, C_6Cl_6, $C_6H_2O_6$ } p. 3474.

$C_6H_6O_2$, p. 3475.

$C_6H_6N_4$, $C_6H_6Cl_6$ } p. 3476.

C_6: C_6H_6S

$C_6H_{15}P$, $C_6H_3OCl_3$, $C_6H_3NCl_4$ } p. 3480.

$C_6H_{20}O_2As_2$, $C_6H_2ONBr_3$ } p. 3489.

$C_6H_{14}O_2NBr$, $C_6H_5OCl_2SP$ } p. 3491.

In the foregoing arrangement, the formulæ are given in the same order as in the *Berichte*, other formulæ which come in between these being omitted; and in the following table these formulæ are re-written and re-arranged on the plan which we have adopted, a few formulæ not found in the *Berichte* index being added to illustrate the application of our scheme to inorganic bodies.

Formulæ Re-written and Arranged on the Plan adopted by the Classification Division, U.S. Patent Office.

The re-written formula is, in our digest, generally followed by the empirical or constitutional formula as usually written by chemists, but from lack of space I have omitted the constitutional formula in many cases in the following table:—

* Read before the Washington Section of the American Chemical Society, May 10, 1900. From the *Journal of the American Chemical Society*, xxii., No. 8.

Not in *Berichte* index.

- $AgCl$
- $AgMnO_4$
- $AlH_4NO_8S_2$ or $NH_4Al(SO_4)_2+12H_2O$
- AsH_2KO_4 or KH_2AsO_4
- C_0 $AuCl_4K$ or $KAuCl_4$
- $BNaO_2$ or $NaBO_2$
- BaN_2O_6 or $Ba(NO_3)_2$
- Br_2OSe or $SeOBr_2$
- Br_2Zn or $ZnBr_2$

- H_0: CBrN or BrCN; $CBr_2N_2O_4$ or $C(NO_2)_2Br_2$; CCl_2O or $COCl_2$; CCl_4
- H_1: $CHBrN_2O_4$ or $CHBr(NO_2)_2$; $CHBr_3$; $CHClO_2$ or $COCl.OH$; $CHCl_3$; CHN or HCN
- C_1: CHNS or CN.SH
- H_2: CH_2I_2; CH_2N_4; CH_2O or COH_2
- H_3: CH_3Br; CH_3N_5
- H_4: CH_4O_3
- H_5: CH_5N or $NH_2(CH_3)$
- H_0: CO_2; CS_2
- H_0: C_2Cl_6; $C_2Cl_6Hg_6$ or $C_2Hg_6Cl_6$
- H_1: $C_2HCl_3Hg_3O_2$ or $CHg_3Cl_3CO_2H$; C_2HCl_3O or $CCl_3.CHO$; C_2HN_3
- H_2: C_2H_2; $C_2H_2ClN_3$; $C_2H_2N_4O_8$ or $C_2H_2(NO_2)_4$
- C_2 H_3: $C_2H_3BrO_2$; $C_2H_3Cl_3O_2$ or $CCl_3.CH(OH)_2$
- H_4: $C_2H_4Cl_2N_2$ or $(CH_2Cl)_2N_2$; $C_2H_4O_7S_2$ or $CHO.CH(SO_3H)_2$
- H_5: $C_2H_5Cl_3N_2$; $C_2H_5NO_2$ or $C_2H_5NO_2$
- H_6: C_2H_6BrN or $N(CH_3)_2Br$; $C_2H_6O_3S$ or $C_2H_5(SO_3H)$
- H_0: $C_2Hg_2I_2$
- H_1: $C_3HN_5O_2$ or
- H_2: C_3H_2O or $CHO.C_2H$
- H_3: C_3H_3BrO; C_3H_5BrO
- H_5: C_3H_5ClO; $C_3H_5N_3O_2S$
- C_3 H_6: C_3H_6 or $CH_3.CH.CH_2$; C_3H_6BrNO or $N.CO.C_2H_5.HBr$; $C_3H_6N_2S$; C_3H_9NO or $OH.CH_2.CH_2.NH.CH_3$
- H_9: C_3H_9NS or
- H_{12}: $C_3H_{12}N_2O$ or $OH(CH_3)_3N.NH_2$
- H_2: $C_4H_2N_2O_4$
- H_4: C_4H_4O or
- C_4 H_7: $C_4H_7N_3OS$
- H_{12}: $C_4H_{12}N_2$ or $(CH_3)_2N.N(CH_3)_2$
- H_{13}: $C_4H_{13}NO$ or $N(CH_3)_4OH$
- $C_4H_4N_2$
- H_1: $C_5HCl_3N_4$
- H_2: $C_5H_2Cl_2N_4O$; $C_5H_2Cl_4O_3$
- C_5 H_4: $C_5H_4O_2$
- H_{11}: $C_5H_{11}N$

- C_5 H_{12}: C_5H_{12} or $CH_3(CH_2)_3CH_3$
- H_{14}: $C_5H_{14}N_2$
- H_{15}: $C_5H_{15}NO_2$ or $N(CH_3)_3(C_2H_4.OH)OH$
- H_0: C_6Cl_6
- H_2: $C_6H_2Br_3NO$; $C_6H_2O_6$
- H_3: $C_6H_3Cl_3O$ or $C_6H_2Cl_3(OH)$; $C_6H_3Cl_4N$ or $C_6H_1Cl_4NH_2$
- H_5: $C_6H_5Cl_2OPS$ or $SP(OC_6H_5)Cl_2$
- C_6 H_6: C_6H_6; $C_6H_6Cl_6$; $C_6H_6N_4$ or ; $C_6H_6O_2$ or $C_6H_4(OH)_2$; C_6H_6S or $C_6H_5.SH$
- H_{14}: C_6H_{14} or $(CH_3)_2CH.CH(CH_3)_2$; $C_6H_{14}Br$
- H_{15}: $C_6H_{15}P$ or $P(C_2H_5)_3$
- H_{20}: $C_6H_{20}As_2O_2$ or $(CH_3)_3(OH)As_2OH(CH_3)_3$

Not in *Berichte* index.

- Cl: ClO_4; Cl_2Ni or $NiCl_2$; CoS
- Cr: CrO_4Pb or $PbCrO_4$; $Cr_2K_2O_{16}S_4$ or $Cr_2(SO_4)_3K_2SO_4+24H_2O$; CuN_2O_6 or $Cu(NO_3)_2$; $FeKO_8S_2$ or $FeK(SO_4)_2$
- H: HK_2 or K_2H; H_2MoO_4; H_3N or NH_3; $HgNO_3$; IKO_3 or KIO_3; $K_2NiO_8S_2$ or $NiSO_4+K_2SO_4+6H_2O$; MoO_4Pb or $PbMoO_4$; Na_2O_3Si or $Na_2S.O_3$
- O: OPb or PbO; O_2Pd or PdO_2; O_3Te or TeO_3
- SSi or SiS

As a practical test of the two systems take the six following bodies, re-write them first by our system and find them in our table; then re-write them by the *Berichte* rules and find them in the *Berichte* table; and the demonstration of the superior simplicity of our system will be complete. The bodies are:—

1. .. .. $SP(OC_6H_5)Cl_2$
2. .. .. $C_6H_2Cl_3(OH)$
3. .. .. $CHg_3Cl_3CO_2H$
4. .. .. CN.SH
5. .. .. $N.CO.C_2H_5.HBr$
6. .. ..

This comparison speaks louder than words, and I think most chemists will agree with me that our system affords to the inquirer with the minimum of technical knowledge the maximum of information, in the surest manner, and with the minimum of mental and physical labour, and without the danger that a future change in theory will mislead the future user of it. In other words, the use of the digest is as far as possible independent of all theory, and founded only on unchanging facts

Let me here call attention to the point that, in the *Berichte* system, the formulæ of very many large classes of bodies—such as salts, amides, anilides of acids, &c.,—have no representation in the index. Their formulæ do not appear in it at all; but only their names, which are classified under the different formulæ of some related body; so that in a given case, unless one remembers all these various classes of excepted bodies, if forgetting any of these things he re-writes the formula, and enters the

Berichte digest or index with it, thus re-written, he finds none of the matter indexed. He must first remember that the body sought is not indexed under its own, but under some different formula of a body more or less closely related to it; that is, that the body belongs in some one of these many excepted classes, and then, after determining under what base or acid it will be found, he must enter the table with the re-written formula, not of the body itself, but of the given base acid or other body to which it is now supposed to be related, although advancing knowledge may hereafter prove this view as to supposed relationship to be erroneous.

Moreover, in the case of a body of which the number and kind of the component atoms are known, but as to the constitution of which little or nothing is known, while the body may be correctly entered in the *Berichte* index under the formula of some base or acid or other supposedly related body, it would evidently never be found, because not knowing its constitution, we do not know the base or acid under which it is indexed, and so would not find it in the table,

In our system, every chemical body indexed is represented in the digest or table by its re-written empirical formula. No bodies are indexed as sub heads under the formulæ of other compounds. The indexing, and conversely, the finding of the body in the index, is rendered absolutely independent of any theories of constitution whatever, and made to depend solely on the kind and number of the component atoms, arranged alphabetically by their symbols, except that in carbon compounds, C comes first and H second. Nothing can be more simple.

No serious attempt is made, however, to make the system, which is merely intended to be a reference index, at once a classification and also an index as well; that is, classification is not pushed beyond the point where it begins to encroach on the digest idea; and any such attempt, I believe, will surely fail to fully fulfil either function in the highest degree. In a good index, the classification idea must be kept subordinate. Hence, it follows that from our point of view, the *Berichte* system, as a mere digest or index, as well as that of Richter and all other similar systems, is inferior to ours in the points indicated; while as systems of classification, they can not but be inferior to such as are founded on proper lines. Such systems can be worked out without being hampered by the digest or dictionary idea, and which important work —classification proper as distinguished from a mere digest or index—we hope to be able to take up at some future time, on a comprehensive scale, as supplementary to the present work in hand.

It would be manifestly unfair, however, in this comparison of systems, to overlook the fact that both in the field covered, and in the intended use, the two systems are not exactly the same. Richter's system is designed for, and applied solely to, the bodies of organic chemistry for the use of specialists in that branch familiar with its classification. Ours covers the entire domain of chemical research, both inorganic and organic, and is for the general inquirer. From a classification standpoint, the order of preference—C, H, O, N, Cl, Br, I, F, S, P—is justified in organic chemistry; but in inorganic chemistry it has no justification, and would lead to awkward and unfamiliar formulæ, with no compensating advantages.

When a general reference index to all bodies, both organic and inorganic, is under consideration, if an order of preference is to be established, one will have to adopt different orders in the organic and inorganic domains, or else do as we have done—that is, establish no order of preference whatever, with the one exception, of giving C and H preference in that order in carbon compounds so as to thereby effect a differentiation of organic from inorganic bodies.

Moreover, Richter's system is more adapted to the needs of those who are studying bodies as a class, and to whom classification is of greater importance; while our system is specially adapted to the needs and requirements of those who are merely searching for references to the literature of specific chemical bodies—particularly those bodies the empirical formulæ of which are known, but as to the constitution of which little, if any, information is at hand.

The approval of our system, therefore, does not necessarily imply that it is a criticism of or shall supersede that of Richter. Because of these differences in the field covered and in the intended use, the two systems have really no serious quarrel; and where ours is applied to organic bodies, the Richter formula could also be given on the cards prepared on our system to facilitate reference to the *Berichte*, and the Richter Lexicon, with its 75,000 titles of organic compounds.

In conclusion, there arises the question of how far the system described in this paper is adapted to the needs of chemists generally as a universal scheme for the indexing or digesting of chemical literature. That it fully meets the needs of the Patent Office we have no doubt, and for myself, I cannot see why the needs of the practical and scientific chemist are not about the same as ours.

The object of a dictionary of chemistry, a reference index, or a digest system, such as those contained in the German *Berichte* and similar works, and the *Abstracts of the Chemical Society*, is to furnish to the chemical inquirer, in the best and quickest way, digested information and references to the latest literature on any given chemical body, process, or general chemical topic. Our system directly covers, very fully, and in, we believe, the best and quickest way, the inquiry as to the chemical body, and incidentally, the inquiry as to any specific chemical process, since every such process has for its aim the production of a specific chemical body, and hence the literature relating to such process will, of course, be digested under the formula of the resulting product.

An index or digest of general chemical topics, or processes of a general nature not specially adapted to the production of a specific body, but to many bodies more or less closely related, can not, of course, be included in any mere formula scheme, which can only represent specific bodies, but must come into some general or dictionary plan based on names or titles, and such references of this class as it might seem desirable to include in a general scheme of chemical indexing, would easily work in with the alphabetical arrangement of chemical names provided for in the system we have adopted.

Probably the most natural objection which the practical chemist would make to the adoption of the system of indexing by re-written formulæ as one of the component parts of a general scheme for chemical indexing, would be that to re-write or re-arrange the chemical symbols in the accepted formula on a purely alphabetical basis, would appear to offend the chemical sense, and do violence to the long-established usage of chemists in writing such formulæ with the component elements or radicals arranged in an order depending largely on their relative, positive, or negative qualities, using these terms in their broadest chemical meaning.

In answer to this objection, it should be noted that if this really be a valid objection, it applies just as fully to the system used by Richter in the earlier additions of his "Lexicon," and adopted and approved in the *Berichte* Indexes, and other publications, as to ours; and it can be urged with equal force against the monumental work of Richter, just published, which is an enlarged edition of his earlier work. So that, with such backing as Richter and the *Berichte*, it would seem as if the objection was not as valid as might at first appear.

Moreover, in our system it is an unvarying rule that the re-arranged formula is never used or written, whether on cards or elsewhere, without being immediately followed by the empirical or constitutional formulæ, so far as the same are known or inferred; so that an objection which might have force, were nothing but the re-written formulæ given in the digest or on the index cards, loses its force when the ordinary formula, so familiar to the chemist, is

always an invariable accompaniment of the new and unfamiliar indexing formulæ.

As soon as the idea is fully grasped that the re-written formula is merely an arbitary arrangement, in the nature of a position indicator, determining position in a mere reference index to literature and nothing more, the chemical sense will be no longer offended. The justification for its use lies in the fact that such a formula unerringly indicates one, and one only, definite and specific place in the index where we are to look for all references, with a certainty that no other character, name, or title of the body can afford. With other systems we are somewhat uncertain where to look for our information; with this system all uncertainty at once disappears.

Personally I should be glad to see a general scheme of indexing current chemical literature carried out at some future time for the benefit of American chemists, under the auspices, for instance, of the Smithsonion Institution, along these general lines which have been blocked out in our Classification Division, modified or improved perhaps by the combined wisdom and experience of the American Chemical Society.

For example, the Smithsonian Institution might publish an annual index to current chemical literature, divided into a formula division, arranged along some such lines as here suggested, and a subject-matter or title division, in which all names and subjects were alphabetically arranged, and the names of chemical bodies all cross-referenced into the formula index, all references to the literature of chemical bodies being collated under the unvarying formula of the body, and not under one of its various and varying names.

Such an index should cover the leading chemical periodicals—such works as *Berichte* and the *Abstracts of the Chemical Society*, and the more important chemical publications of the year.

The vast army of chemical workers in our universities, laboratories, and corporate and government offices and institutions, state and national, should be enlisted in the work, each willing worker assigned some special publication or portion of same, and be supplied with standard library bureau cards and general instructions; and the cards as prepared sent in to the central bureau established here in Washington, where, after being sorted into place in the receiving cabinets, and with proper editing, they would form the basis from which would be compiled the annual index volume.

These volumes would probably be less of a digest and more of an index than the present *Abstracts of the Chemical Society* or the *Berichte*, and would cover a somewhat different field than either.

Lastly, these annual volumes should be sold at cost price, so as to become a working tool in the hands of all the chemical workers in the country.

I may here briefly refer to a special development of this work now being carried out in our Patent Office Index. We have procured two copies each of the *Berichte* Indexes for 1898 and 1899. The separate titles in the formula portion of these indexes are in most cases small enough to be cut out and pasted on our standard indexing cards, and still leave room enough at the top to re-write the formula on our own plan. We are also considering the application of this system of cutting and pasting from two duplicate copies to the new Richter "Lexicon" with its 75,000 titles, and possibly to the four volumes of the last edition of Watts's "Dictionary," Thorpe's "Dictionary of Applied Chemistry," the yearly abstract volumes of the *Journal of the London Chemical Society*, and such other works of general reference as it may be found advisable.

But to return, in conclusion, to the idea of a central bureau at Washington, supervising the indexing of chemical literature, would not some such plan, properly matured, and carried out to a successful completion, be a work worthy of the great scientific institution of the national capitol, founded expressly for the dissemination of useful knowledge, and be directly in line with their publication in past years of the indexes to the literature of specific chemical bodies, which has so much redounded to their credit? It seems to me at least that it would be a work worthy of their best endeavour, and of whose great utility there could be no question whatever.

CATALYSIS IN CONCENTRATED SOLUTIONS.*

By J. M. CRAFTS.

(Concluded from p. 207).

B. *Experiments with Metaxylenesulphonic Acid Heated with Sulphuric Acid at 100°.*—

XV. Ten grms. metaxylenesulphonic acid + 35 grms. dilute sulphuric acid (25 per cent H_2SO_4) were heated twenty hours at 100°. There was no sign of separation of xylene.

XVI. Ten grms. metaxylenesulphonic acid + 112 grms. dilute sulphuric acid (50 per cent H_2SO_4).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	4·2	56	69·6
8	13·9	60	71·4
12	21·2	64	74·4
16	27·8	68	76·3
20	34·5	72	78·1
24	40·6	76	79·3
28	44·2	80	81·7
32	47·8	96	85·4
36	52·7	112	86·0
40	56·3	128	87·2
44	59·3	144	88·4
48	64·2	160	88·4
52	66·6	176	88·4

XVII. Ten grms. metaxylenesulphonic acid + dilute sulphuric acid (75 per cent H_2SO_4).

Soon after heating, the well known phenomenon took place between the diluted sulphuric acid and the sulphonic acid; a lighter layer of a viscous liquid rose to the top, and this was covered by a smaller layer of xylene. The viscous layer which separated contained 5·5 per cent of dissolved xylene, and the remainder had nearly the composition $H_2SO_4 + 2H_2O$ (33 per cent) + $C_8H_{10}SO_3 + 2H_2O$ (67 per cent). It is more probable, however, that most of the water should be regarded as combined with sulphuric acid, and the greater part of the metaxylenesulphonic acid must be anhydrous, on account of its power of dissolving xylene. This view is confirmed by the fact that the crystalline hydrated sulphonic acid dissolves on gently warming in sulphuric acid diluted with enough water to make 75 per cent H_2SO_4, and then an acid separates later on heating, giving the upper viscous layer.

These experiments suggest the idea that all dehydrating agents may bring the crystalline hydrated sulphonic acids into an anhydrous state, and that the anhydrous form may exist in solution, and perhaps be more susceptible of hydrolysis than the hydrated acids. This hypothesis will be investigated.

C. *Metaxylenesulphonic Acid Heated to 100° with Nitric Acid.*—

XVIII. Ten grms. metaxylenesulphonic acid + common nitric acid, diluted with an equal weight of water, were heated three hours at 100° in a sealed tube. There was no sign of xylene, and only traces of insoluble nitro-derivatives. The pressure of gas due to oxidation was not very strong.

Thus, nitric acid has no action favouring hydrolysis to be compared to that of a molecular equivalent of chlorhydric or sulphuric acid.

* *Journal of the American Chemical Society*, xxiii., No. 4.

The Relation between Concentration of the Acid Solutions and the Rapidity of the Hydrolysis.

Curves were plotted of all these series of experiments, and the accompanying table gives the time required in each case to decompose 5, 10, 15, &c., per cent of the sulphonic acids.

In Experiments II. to XVI., the first vertical column of the table gives the percentages by weight of HCl gas in the chlorhydric acid solution; the second column gives the weights of acid solution to which in each case 10 grms. of crystallised sulphonic acid were added; and the third vertical column gives for Experiment IV. a weight of H_2SO_4 added to the solution, while for Experiments V., XIII., and XVI. weights of $ZnCl_2$ were added.

The next eighteen vertical columns give the hours and decimal fractions of an hour required to decompose 5, 10, 15, &c., per cent of the sulphonic acid.

The last column gives the velocity constants, calculated, not from the figures of the table, but from the means of the constants given by each experimental measure, rejecting those of less than 10 and more than 80 per cent decomposition, because at the two extremities the results are less accurate.

A very remarkable relation appears between the velocity constants and the concentration of the chlorhydric acid which promotes the action (as a catalysor ?).

For the percentages of HCl between 13 and 31 the velocity increases fourfold for each successive increment of 6 per cent HCl. The rate appears to be less rapid for higher percentages, but the upper limit of the law may perhaps be extended by more careful measures. Unpublished experiments confirm this relation for other sulphonic acids and extend it to lower percentages of HCl.

Mathematically stated, the relation is expressed by the formula: the logarithm of the velocity constant is a linear function of the percentage concentration of chlorhydric acid.

Since the sulphonic acids have nearly as strong a chemical affinity as chlorhydric acid, it was thought that they might catalyse themselves, and the decomposition might be related to the concentration. Only two experiments have been made, but they serve to confirm this idea:—

1. Five grms. metaxylenesulphonic acid were dissolved in 2·5 grms. of water, and were heated at 100° for forty hours. The sulphuric acid set free was 1·9 per cent of the amount corresponding to complete decomposition. No xylene was visible in the tube, but it separated out on diluting with water.

2. Five grms. of metaxylenesulphonic acid were dissolved in 100 grms. water and heated to 100° for forty hours. The sulphuric acid set free was only 0·1 per cent. Thus, concentration in these experiments gives rise to a rapidly increasing rate of decomposition.

With metaxylenesulphonic acid a change of position of the SO_3H group, if such change can be brought about catalytically, would complicate the reaction, since the susceptibility to decomposition is greatly increased when the SO_3H group is placed between the two side chains.

The series of experiments will be extended to other temperatures, and the more tedious—but likewise more accurate—method of weighing the sulphuric acid set free instead of measuring the amount of hydrocarbon will be used.

If we attempt to estimate the differences and the similarities in the modes of catalytic action of strong acids in concentrated or in weak solutions, it will be convenient to do so under the headings of Ostwald's definition of catalysis.

1. *Reactions which are Accelerated or Retarded by Catalysis take place also without a Catalysor.*—Experiments are evidently impossible with substances which take years for the transformation of 1 per cent, and conclusions can usually only be drawn from the form of reaction curves of measurable velocities, but it appears probable that the regularity of the decomposition of sulphonic acids without by-products will make it possible to obtain

PERCENTAGE DECOMPOSITION OF METAXYLENESULPHONIC ACID HEATED TO 100° WITH CHLORHYDRIC ACID.

	Percentage Weight of chlorhydric acid.	Weight of liquid. Added.		Per cent. 5.	10.	15.	20.	25.	30.	35.	40.	45.	50.	55.	60.	65.	70.	75.	80.	85.	90.	Velocity constant. Unit of time, 100 hours.
		Grms.	Grms.																			
II.	13·0	75	—	55·0	118·0	182·5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0·089
III.	19·0	70	—	17·0	29·0	44·0	61·0	80·0	100·0	120·0	140·5	162·0	187·0	210·0	234·0	264·0	—	—	—	—	—	0·39
IV.	10·0	30	8·75 H_2SO_4	13·0	25·0	40·0	55·0	70·5	92·0	113·0	132·0	151·5	170·0	189·0	207·0	233·0	—	—	—	—	—	0·40
V.	19·0	93	37·5 $ZnCl_2$	4·5	6·5	10·0	14·0	18·5	24·0	30·0	37·5	—	—	—	—	—	—	—	—	—	—	1·43
VI.	25·0	45	—	5·0	8·0	11·0	14·5	18·5	23·0	28·0	33·5	39·0	45·5	52·0	58·5	65·5	73·5	84·0	92·0	—	—	1·59
VIII.	31·4	35	—	—	—	4·2	5·3	6·4	7·6	9·0	10·3	11·6	13·0	14·6	16·4	18·5	20·8	23·3	25·8	29·1	—	5·75
IX.	31·4	50	—	0·8	—	2·2	3·6	5·0	6·6	8·3	10·0	11·9	13·9	15·4	16·8	18·0	—	—	—	—	35·0	5·10
X.	38·4	35	—	—	—	—	—	—	—	—	4·0	4·5	5·0	5·5	6·1	6·8	7·5	8·5	9·5	10·8	—	14·1
XI.	38·4	38	—	0·5	1·2	1·6	2·1	2·6	3·1	3·8	4·3	5·0	5·6	6·4	7·1	8·1	9·4	11·2	14·3	—	—	12·9
XII.	43·0	39	—	—	—	—	—	—	1·8	1·95	2·1	2·3	2·6	2·8	3·2	3·7	4·6	5·7	—	—	—	31·0
XIII.	38·4	38	19 $ZnCl_2$	—	—	0·8	0·9	—	1·0	1·2	1·4	1·5	1·7	2·0	2·2	2·4	2·6	2·9	3·4	—	—	47·8
				When Heated to 80·1° with Chlorhydric Acid (38·4 per Cent) and 50 per Cent $ZnCl_2$.																			
XIV.	38·4	36	18 $ZnCl_2$	4·0	6·0	7·6	9·4	11·0	12·8	14·6	16·4	18·3	20·5	22·6	25·0	27·4	30·6	33·6	—	—	—	3·2
				When Heated to 100° with Sulphuric Acid (50 per Cent).																		
XVI.	50·0	35	—	4·0	6·0	8·25	11·0	14·0	17·0	20·5	24·0	29·0	33·5	38·5	44·0	50·0	57·5	65·5	76·5	94·0	—	2·1

useful observations near the border line, where the action is almost imperceptible.

2. *Reactions in Opposite Directions leading to an Equilibrium must be Equally Influenced by Catalysis.*—The hydrolysis of sulphonic acids in presence of sulphuric acid and water would belong under this rule if the reaction were reversible; but this is probably not the case, since the synthesis is direct, while the decomposition is indirect by influence of H_2SO_4 (catalysis?). The data for 50 per cent sulphuric acid given in the preceding table show that the limit of the action is very near complete decomposition (88 per cent), while experiments made by heating xylene with sulphuric acid of 50 per cent concentration to 100° proved that the reverse action does not take place perceptibly.

Even the action of a 75 per cent sulphuric acid solution on xylene is an exceedingly slow one, and stops when only a few per cent of the xylene are transformed into the sulphonic acid. The hydrolysis of sulphonic acids by means of chlorhydric acid tends to complete decomposition, nor can any evidence be obtained of an inverse reaction.

3. *The Catalytic Influence is nearly Proportional to the Concentration of the Catalysor.*—The chief object of this paper is to show that this rule does not apply to the case of concentrated acids, and that here the facts are directly opposed to the assumption that hydrolysis is caused by hydrogen ions. In the experiments cited, the relation between concentration of acid and effect rises like the tension of a gas partially combined with water, and the effect of high concentration in aqueous solution of chlorhydric acid alone, and especially with addition of zinc chloride, recalls the activity imparted to gases condensed on platinum or palladium. Ostwald discusses the action of these metals under the same heading as catalysis attributed to the ions of hydrogen, iron, manganese, &c., and OH ions, and also places ferments and enzymes beside them, saying there is no great doubt that the laws governing the action of these bodies are not essentially different from those of inorganic catalysors.

Taking these definitions together, they apply in very few points to the case of hydrolysis by concentrated acids.

The question of ionic dissociation presents new aspects in this case. Usually the compounds subjected to catalysis have been, like sugar and esters, incapable of any marked degree of dissociation in aqueous solution. The sulphonic acids, on the contrary, are dissociated to nearly the same degree as the strongest acids, when in dilute solution, and although very little is known of the dissociation of strong acids in concentrated solution, it well may be considerable. If hydrolysis only takes place upon undissociated molecules, then the increased rapidity due to high concentration of the acid solution and to addition of zinc chloride may be ascribed to the prevention of the dissociation of the catalysed body, while that of the catalysor subsists to a certain degree.

Experiments at different temperatures and with more sensitive bodies, like mesitylenesulphonic acid, which acts at low temperatures and with weaker acids, may throw some light upon this subject.

The usefulness is evident of a minute study of the difference of behaviour of the sulphonic acids, for it may obviously lead to methods of separation of the hydrocarbons and the acids. Several authors have described such methods for the separation of meta- and paraxylene, and I have found during this series of experiments that mesitylenesulphonic acid, when heated to 80° for fifteen minutes with 38 per cent chlorhydric acid, is almost wholly decomposed, while pseudocumenesulphonic acid, heated under the same circumstances, gives no sign of the separation of pseudocumene after five hours. Armstrong has used this difference of action to separate the two hydrocarbons by heating their sulphonic acids with chlorhydric acid at 100°, but the statement attributed to him in "Beilstein" (II., 29) is incorrect, namely, that pseudocumenesulphonic acid is not decomposed by heating for one hour with strong chlorhydric acid at 100°. There is difficulty in getting the rate for the first hour, because the pseudocumenesulphonic acid does not dissolve rapidly in strong chlorhydric acid at 100°, but the following determinations show the rate for subsequent hours:—

Ten grms. pseudocumenesulphonic acid, heated to 100°, with 35 grms. chlorhydric acid (38·4 per cent HCl), gave the following results:—

Pseudocumene.		Pseudocumene.	
Hours.	Per cent.	Hours.	Per cent.
1½	24·7	6½	95·9
2½	42·3	7½	101·6
3½	61·8	8½	103·8
4½	76·6	9½	100·3
5½	90·5	10½	100·3

The impossible results, 103·8 per cent, &c., may be due to the fact that a small amount of anhydrous sulphonic acid separates out and dissolves in the layer of hydrocarbon, and is only slowly decomposed. All the results are too high for the same reason, and a similar error, but a very small one, attaches to the preceding experiments with xylene. The fact that pseudocumenesulphonic acid loses a little water on long standing may also account for the above result.

Armstrong's observations were undoubtedly exact, but he is misquoted by Beilstein. He really states (*Ber. d. Deut. Chem. Ges.*, xi., 1697) that an oily layer is formed by adding water to the immediate product of the action of sulphuric acid upon pseudocumene, and this oil, added to an equal volume of common chlorhydric acid, is not decomposed by heating one hour to 100°. No strength of acid is given, but the oily layer so described contains anhydrous pseudocumesulphonic acid in solution in aqueous sulphuric acid, and the water present probably suffices to dilute the acids to the point where no perceptible decomposition takes place during one hour at 100°.

The name catalysis has been used after much hesitation, and it is only meant to imply that the rapidity of the action does not seem to be determined by the ordinary chemical forces of the bodies undergoing change, but rather that these forces are set in action in a peculiar way by an outside agent.

THE USE OF ALUMINIUM AS AN ELECTRICAL CONDUCTOR.

The high price which copper has attained during the past few years, owing to a combination of natural and artifical causes, has drawn attention to the use of aluminium as an alternative conductor for the transmission of electric energy.

In order to make a proper comparison between copper and aluminium, from the point of view of their cost, we must take into consideration their densities and their different conductivities. If we take the average for the two metals in France, we arrive at the conclusion that, for equal conductivities, an aluminium line will cost 1000 francs, while a similar line of copper would only cost 798 francs. Aluminium is therefore dearer than copper in this country.

In America, however, considerable quantities of aluminium have been sold within the last few years at a very low price, which brings the ratio between copper and aluminium to $\frac{1325}{1000}$ for an equal conductive capacity; this fact explains the facility with which the electricians of the New World have been able to adopt the white metal as a conductor. It must be remarked, however, that at the present time, and until the price has fallen considerably lower with regard to copper, there can be no question of using aluminium for a covered insulated conductor; still it is already in great demand for aërial lines.

The following are the details of some of the pure aluminium cables already installed on the other side of the Atlantic :—

At the Falls of Niagara there are two aluminium conductors. These two lines are short, and are known to give very satisfactory working results.

The Hartford Electric Light and Power Company has an aluminium line from its central station at Tariffville to Hartford, a distance of 17·7 kilometres. The diameter of the cable used is 0·0187 metre, and it weighs about 422·5 kilogrms. per kilometre.

The aluminium conductor belonging to the Snoqualmie Falls Power Company has been frequently described in the technical press. It runs from the Falls to the two towns of Tacoma and Seattle. Its total length is 54·716 kilometres. The aluminium used was alloyed with 1·5 per cent of copper, and the increased tenacity obtained by this alloy permitted the safe use of cables of 36·5 m.m. to 45·6 m.m.

The Blue Lakes Power Company has an aluminium conductor in use between its central station at Blue Lakes and Sockton, a distance of 57·934 kilometres. The original line has been replaced by a new one of greater conductivity; 446 tons of metal were used for the new line. At 1 fr. 45 centimes per pound, this represents a total of 1,510,000 frs. (or 41,925 frs. per mile) for the metal alone.

One of the most interesting systems for the transmission of power in the United States, in which aluminium is used, is that of the Telluride Power Company.

This company produces its current at Provo in Utah, and distributes it through a circuit of 128·75 kilometres to the mines at Mercur and Tintic.

The following are the names of a few other American companies in which aluminium is used, or is on the point of being substituted for copper :—

1. The North Yuba Power Company, 101·385 kilometres ;
2. The Municipal Supply Company, 28·967 kilometres ;
3. The Big Cotton Wood Power Company ;
4. The Standard Electric Company.

This latter company has been invited to instal a plant to supply San Francisco with electricity from a generating station to be situated in the mountains of Sierra Nevada, at a distance of over 240 kilometres away.

The success of this project depends on the possibility of maintaining the tension of 60,000 volts.

It has been decided to use aluminium cables for the purpose, and the plans have all been prepared.

In the greater number of these installations the difficulty of soldering the aluminium has been overcome by the use of mechanical joints. The MacIntyre sleeve joint has been generally adopted.

An examination of the principal installations where aluminium is used as a conductor shows the very great progress that has been made.

If this metal is sufficiently durable, and if its price continues to diminish, it will doubtless become an important rival to copper in this new field of usefulness.—*Révue Générale des Sciences*, Year XII., No. 19, October 15th, 1901.

THE ESTIMATION OF PLATINUM AND IRIDIUM IN PLATINUM ORES.

By MM. LEIDIÉ and QUENNESSEN.

THE method devised by M. E. Leidié for the extraction and separation one from the other of the metals of the platinum group is of a general character, but it is principally intended for the solution of the most difficult cases in which the material is more or less completely insoluble in the solvents usually employed (*Comptes Rendus*, vol. cxxxi., p. 888; *Bull. Soc. Chim.*, [3], vol. xxv., p. 9).

A much more simple case occurs in practice ; that is to say, on the small scale the estimation of platinum in its ores, and on the large scale the commercial extraction of platinum. M. Leidié's method can be simplified, therefore, in the following manner :—

To obtain the metals in the form of chlorides we attack the ore with hot aqua regia (nitric acid D=1·32 1 part, and hydrochloric acid D=1·18 3 parts), until nothing more can be dissolved; the solutions are then evaporated, first on a sand-bath until they are of a syrupy consistence, then in a Wiessnegg oven at 105—110° until quite dry ; the residue is taken up with water and filtered.

The method described by M. Leidié is then applied. We will briefly describe this method. The solution, heated to about 70°, is treated with nitrite of sodium until neutral to litmus, then with carbonate of sodium until no further precipitate is formed; it is then boiled, and filtered to separate all the metals which do not belong to the platinum group. A current of chlorine is then passed through the solution, which has been made alkaline with soda ; then heat to 70—80° ; this drives off the osmium and ruthenium in the form of volatile peroxides. The solution is neutralised with hydrochloric acid, and a further quantity of nitrite of sodium is added to re-form the metals which may have been partially transformed into chlorides, into nitrites.*

Estimation of the Platinum.—Instead of now saturating the solution with chloride of ammonium, as in the original process, we add chloride of potassium (about 30 to 35 per cent); the rhodium and iridium are precipitated in the state of double nitrites of potassium, which are insoluble in solutions of alkaline chlorides, like the corresponding nitrites of ammonium. The solution is then filtered, and the nitrites of platinum and palladium are transformed into chlorides by means of hydrochloric acid, taking the precautions that have already been pointed out. The saline mass is taken up with boiling water. The solution, containing platinum and palladium in the state of double chlorides, is then made alkaline with a little soda, and boiled in the presence of a slight excess of formol, so as to precipitate the two metals in the *black* or metallic form ; the precipitate is collected on a filter, calcined, reduced with hydrogen, and then taken up with aqua regia. The solution is evaporated down and taken up with water, then treated with NH_4Cl to precipitate the platinum. This metal is then estimated by any of the ordinary known methods.

This modification of M. E. Leidié's original method was devised for the purpose of doing away with the driving off of the chloride of ammonium by heat, an operation which is attended by a good deal of trouble when operating on the large scale, and which may easily be accompanied by a loss of the metal if it is not very carefully carried out. Further, the reduction by formol cannot be effected in the presence of NH_4Cl, as the evolution of ammonia, caused by the action of the soda, transforms the salts of palladium and platinum into palladoamines and platinoamines. Now, as these ammoniated bases cannot be reduced either by formol, or even by the dissolved alkaline formates, it is necessary, for separating the whole of the metals, to evaporate the whole to dryness with a formate —and that several times over—as done by Ste.-Claire Deville and Debray ; thus we should only come across another set of difficulties.

* It can be seen that all the foreign metals are completely precipitated, and that the metals of the platinum group are completely transformed into double nitrites, by the fact that the filtrate no longer gives a precipitate in the cold with sulphydric acid. It may happen in a case when large quantities of nitrite have been used, that a little copper will remain in solution; this metal would then be in the form of a *cuprous* salt not precipitable under these conditions. We then add a little peroxide of hydrogen to the solution and heat to boiling-point ; the cupric oxide formed is then entirely precipitated. In the operations which follow it is necessary to avoid too great concentration of the solutions, as some platinum might then be lost. The solution is of a convenient degree of concentration when it only just commences to crystallise at the edges ; a little water can then be added to just dissolve these crystals.

Estimation of the Iridium.—As to the double nitrites of rhodium and iridium formed with the potassium, they are not well adapted to the estimation of these two metals, inasmuch as they are more difficult to decompose with hot hydrochloric acid; and, further, the double chlorides thus obtained are very slightly soluble. Therefore, when it is a question of estimating iridium, it is necessary to divide into two parts the solution from which the osmium and ruthenium have been driven off. The first part should be treated, as has already been described, by KCl for the estimation of the platinum; the second part should be treated with NH_4Cl.

The double nitrite of ammonium and rhodium, as well as that of ammonium and iridium, are transformed, on the other hand, much more easily by aqua regia containing only a little nitric acid, into Rh_2Cl_6 and $IrCl_4$. The iridium is precipitated in the form of chloroiridiate by NH_4Cl, with which the solution should be saturated; this precipitate is collected on a filter, washed with a solution of NH_4Cl, and calcined. The metal is then reduced by hydrogen and weighed.

We could also precipitate the $IrCl_4$ by KCl in the state of chloroiridiate, $IrCl_4.2KCl$, by saturating the solution with KCl. By adding to the solution a little chlorine water, which does not act on the KCl as on NH_4Cl, the precipitation is more rapid. The product of the reduction is washed with water, to remove the chloride of potassium, and dried at 105°.

This method, when carried out as described, is fairly rapid. It as is well to operate on at least 5 grms. of mineral for each assay.

While the general method of M. E. Leidié gives all the iridium contained in the ore or in the residues, in whatever state it may exist, the present method will not give the iridium which is present in the form of osmide of iridium, as this latter is insoluble in aqua regia. It gives the iridium alloyed with the other metals; we know, in fact, that when it is in the form of an alloy, iridium is soluble in aqua regia, and in ordinary ores it is not found in the free state in sufficiently large quantities to remain undissolved.

The extraction of the iridium from osmide of iridium is, commercially, the subject of a special operation, entirely different from the extraction of iridium from platinum ores.

We propose to apply this modification of the original method to the commercial extraction of platinum and iridium, and to work out the practical and economic conditions of this application.—*Bull. Soc. Chim.*, Series 3, xxv., No. 18.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, October 25th, 1901.

Prof. S. P. THOMPSON, President, in the Chair.

A PAPER "*On the Variation with Temperature of the Thermoelectromotive Force and of the Electric Resistance of Nickel, Iron, and Copper between the Temperatures of* $-200°$ *and* $+1050°$" was read by Mr. E. P. HARRISON.

In this paper the changes with temperature of the thermoelectric force and the resistance of nickel and iron are traced over a wide range, and the singularities present in the curves representing these changes are investigated. In all experiments the same specimens of metal were used. Previous work on this subject has been performed by Tait, Fleming and Dewar, Holborn and Day, and Stansfield. In the author's experiments on E.M.F. an ordinary potentiometer method was used, the potential difference due to the thermo-couple being balanced against a portion of that due to two accumulators. Before each reading a standard cadmium cell was balanced on a definite resistance in the accumulator circuit. Readings of E.M.F. of copper-nickel couples were accurate to 1·8 microvolts, while those of copper-iron couples were accurate to less than one microvolt at moderate temperatures. The heating arrangement was designed to give a uniform temperature which was measured by a platinum thermometer, and recorded automatically by Callendar's recorder. The cold junctions were placed in a large test-tube full of water; the test-tube was placed in a larger vessel also containing water. The temperature of the cold junctions varied with that of the room, and all observations were reduced to cold junction 0° C. Finally, in each case, observations were taken by placing the junctions in liquid air with the platinum thermometer beside them. To prevent oxidation of the metals forming the junctions at temperatures, above 500° it was necessary to exhaust the porcelain tubes which contained them. The curves for variation of E.M.F. with temperature of copper-nickel and copper-iron couples are roughly a straight line and a parabola respectively. The differences between the actual curves and a selected straight line in the former case and a parabola in the latter case have been plotted against temperature. These difference curves show that the maximum variations occur in the case of copper-iron, at 70°, 230°, and 370°. The temperature of inversion (cold junction 0° C.) is 536° C., and the neutral point is 262° C. In the case of copper-nickel maximum variations occur at 70° and 340°, and there appears to be a small hysteresis effect at the latter point. The temperature of inversion does not occur within the limits of the experiments, and there is no neutral point. The E.M.F. curve for a nickel-iron couple up to 700° has been obtained from the two previous experimental curves by addition. Above this temperature direct observations have been taken. This curve is nearly linear up to 900°, at which point a decrease in E.M.F. occurs. Curves of thermoelectric power have been derived from the E.M.F. curves by drawing tangents, and these show that a considerable range of the copper-iron curve can be represented by straight lines, but that the remainder is approximately parabolic. The copper-nickel power curve can be represented by bits of straight lines. The Peltier-coefficient variation curve for iron-copper is at first parabolic, and can then be made up of straight lines; for copper-nickel it can be made up of bits of parabolas. Considerable difficulty was experienced at high temperatures in getting concordant results owing to chemical changes and other effects. The experiments were therefore carried out under different conditions, and the results are discussed in the paper.

In the resistance experiments a potentiometer was employed, a manganin resistance coil immersed in an oil-bath being used as a standard. The resistance of nickel increases with temperature almost parabolically up to 370°, when a change of slope occurs, and the resistance increases much less rapidly and almost linearly up to 1050°. In the case of iron, the resistance curve does not change its parabolic form till nearly 800°, when it becomes linear, and remains so up to 1050°. The author concludes from his paper that the thermoelectric change in nickel-copper coincides approximately with the resistance change, but that no thermoelectric peculiarity exists for iron-copper at the temperature of the iron resistance change.

Mr. A. CAMPBELL said that with purer iron the change in thermoelectric properties might correspond with the change in resistance. Dr. Knott had performed experiments on nickel in 1886, and got results similar to those of the author. His results with thick wires were different to those with thin, probably because he did not exclude air and prevent oxidation. Mr. Campbell said that he had himself made experiments upon two samples of nickel differing in resistivity, and although their temperature coefficients were also different, the change in slope of the curve connecting resistance and temperature occurred at practically the same temperature in both specimens.

Their thermoelectric powers were identical up to 300°, but above they differed slightly.

Dr. D. K. Morris pointed out that the thermoelectric force, the resistance, and the magnetic properties should be observed at the same time. In taking a thermoelectromotive force there must be a temperature gradient, and in the interesting parts of the curves differences of magnetic properties may arise and produce discrepancies. He drew attention to the caution which must be exercised in differentiating by drawing tangents except when the curves are smooth. Dr. Morris said the connection between resistance and magnetic qualities was interesting. The temperature coefficient of resistance of a magnetic body rises with temperature so long as the body is magnetic, but reverses when the body becomes non-magnetic. He asked for information on the subject.

Prof. H. L. Callendar said he had followed the research with interest, and referred to the experimental difficulties, especially at high temperatures. He should like to have said something in reply to Dr. Morris, but he was afraid the subject was a large one, and might well be discussed at some future meeting. There were several points to clear up, and the fact that the curves described cannot be represented by straight lines or parabolas showed that the subject was beyond the range of a simple theory.

The Chairman suggested that it might be well to re-examine more carefully some of the curves which are accepted as straight lines, and on which there is no complication due to magnetic properties. He hoped the author and others would continue working at this subject.

Mr. E. P. Harrison, in reply to Dr. Morris, said he thought the number and accuracy of his observations justified him in drawing tangents to form his power and Peltier effect curves.

A paper on "*Asymmetry of the Zeeman Effect*," by Mr. G. W. Walker, was read by the Secretary.

Professor Voight predicted an asymmetry of the normal triplet, which has been verified by Zeeman. The author has considered the subject mathematically, and finds that asymmetry may arise as a second order term due to the magnetic field. The asymmetry would be more distinct the greater the field, which is opposed to the theory of Voigt. By giving numerical values to the symbols it is shown that the effect is extremely small. The author points out that his theory can provide an explanation of why a line may not be resolvable.

The Society then adjourned until November 8th, 1901.

NOTICES OF BOOKS.

Smokeless Powder, Nitrocellulose, and Theory of the Cellulose Molecule. By John B. Bernadou. New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1901. viii.—200 pp. 12mo.

The author and compiler of this neat volume is a lieutenant in the United States Navy, and dates the preface on board the U.S.S. "Dixie." He has brought together for the purpose of comparative study several essays by distinguished authors; to wit:—Two papers on "The Nitration of Cotton," by M. Vieille and by M. Bruley; "Pyrocollodion Smokeless Powders," by D. Mendeleeff; and the "Development of Smokeless Powder," by the author of the work. These are prefixed by original chapters on the theory of the cellulose molecule, and earlier views as to the composition and constitution of nitrocellulose, as well as a very clear presentation of the origin, nomenclature, and definitions of the diverse bodies of the nature of explosives used in military operations.

Lieutenant Bernadou has himself pursued chemical and military (or naval) researches for many years, and embodies in his treatise the results which confirm those of others, and at the same time throw much light on them, showing their interdependence. His experiments conducted at the Naval Torpedo Station, Newport, resulted in the preparation of a new form of nitrocellulose capable of being converted directly by colloidisation into a smokeless powder suitable for arms of all calibres. This is now manufactured on a commercial scale in several establishments. And one of the objects of the book announced by the author is to prepare the way for the introduction of future improvements in progressive explosives.

Besides the chemical side of the question, the author treats of the ballistic values and properties of the products.

The volume can be commended to students of military and naval problems involving the use of explosives.

H. C. B.

A Short Manual of Inorganic Chemistry. By A. Dupré, Ph.D., F.R.S., &c., and H. Wilson Hake, Ph.D., F.C.S., &c. Third Edition. London: Charles Griffin and Co., Limited. 1901. Pp. 391.

This new edition of the "Manual of Inorganic Chemistry," while retaining the main features of the preceding editions, has been at the same time thoroughly revised and partly re-written with special reference to the periodic law.

It is of importance that a student who has no previous knowledge of chemistry should be first grounded in the general principles which govern that science; with this object in view the authors have dealt, in the introductory portion of the book, with these general principles, and it is intended and hoped that this part should be read straight through before proceeding to the description of the properties of the various elements and their compounds.

The "Scheme of Properties" (p. 101) has been adhered to for the systematic and uniform arrangement of facts relating to the various elements and compounds. This scheme has been found to be of great convenience, and is already becoming well known.

The chapter on the "Periodic Law" goes very fully into the history and development of the scheme devised by Mendeleeff, though the atomic weights used by Mendeleeff do not always agree with the exact figures used in the text of this work.

In the second part of the book, "Some Typical Elements and their Compounds," a certain number of elements are first dealt with and fully described; they are then all considered *seriatim*, in the group arrangement laid down by Mendeleeff; this comprises eight groups, followed by the transition elements of Group I., viz., Cu, Ag, and Au.

We would, however, point out to the authors that, valuable and important as Mendeleeff's arrangement is, other more modern and more comprehensive arrangements have since been published, and we should at least expect them to be mentioned in a work that claims to be "thoroughly revised and partly re-written, with special reference to the periodic law."

The appendix contains some useful tables and additions, such as a paragraph on Gay-Lussac's "Law of Volumes," which should have been inserted in Chapter X., but was accidently omitted. There are also Tables of the Thermal Values of Typical Chemical Reactions, the Heat of Neutralisation of some Acids and Bases, the Relative Avidity of Acids, &c. There is a full table of contents, and a good index of twenty-six columns.

Select Methods in Food Analysis. By Henry Leffmann, A.M., M.D., and William Beam, A.M., M.D. With fifty-three Illustrations in the text, four full-page Plates, and many Tables. Philadelphia: P. Blakiston's Son and Co. 1901. Pp. 383.

As a concise summary of analytical methods for the use of both practical analysts and students this volume cannot fail to be of great value.

Great strides have been made in food analysis during

the past ten or fifteen years, but much of this information has been published unsystematically in reports and isolated papers, &c.

In the present work the authors have collected and arranged these methods as far as possible, including many of the most recent processes and results.

The effects of food adulteration and the methods of controlling it have not been given any consideration, as these topics do not appear to concern the analyst, but special attention has been given to the detection of preservatives, artificial colours, and poisonous metals.

The first and shorter part of the book deals with general analytical methods, such as specific gravity, boiling-points, polarimetry, microscopy, &c., with a short description of the apparatus and chemicals used. The second part on "Applied Analysis" contains, first, the general methods to be adopted, such as those for detecting poisonous metals, colours, &c., followed by a large section devoted to special methods of food analysis; these include methods for the analysis of starchy matters, fats and oils, milk and milk products, non-alcoholic beverages, such as tea, coffee, and cocoa, condiments and spices, alcoholic beverages, and flesh foods, including meat extracts.

The appendix contains some useful tables, and is followed by four full-page plates, two of which illustrate the appearance of various substances under the microscope, such as arrowroot, wheat, pea, rice, maize, ginger, buckwheat, &c.; while in the other two we have illustrations of the genuine tea-leaf (*Thea chinensis*), and twenty-one other kinds of leaf which are mixed with it for purposes of adulteration.

The book is well written, printed, and bound, and contains a comprehensive table of contents as well as a good index.

CORRESPONDENCE.

ON THE EXISTENCE OF A NEW ELEMENT ASSOCIATED WITH THORIUM.

To the Editor of the Chemical News.

Sir,—The last two numbers of the Chemical News (October 11th and 18th) contain a paper by Mr. Charles Baskerville "On the Existence of a New Element Associated with Thorium." The author says in a footnote that he wrote to me of his observations during the fall of the last year, and that he was surprised to observe in the *Proc. Chem. Soc.* of April 10th my article in which I give good evidence of the complexity of thorium, dividing that element into Th_α and Th_β.

Mr. Baskerville's letter really reached me in February, 1901, and it contains the following passage:—

"I may say I think that I have broken thorium up into two elements, but this may turn out in the end like so many other efforts to decompose many of our well known elements."

Absolutely no word more is said on the method used or the results obtained.

I confess myself guilty of not having answered this letter, at the receipt of which I could not but feel "*Noli turbare circulos meos!*" Perhaps an explanation may be found in the circumstance that at that very time I was engaged in reviewing the results of my work on the complex nature of thorium, which had occupied me during the last five years,* and of a work on some other rare earth metals, in order to communicate it to the Chemical Society; this was done in an exceedingly condensed form in March, 1901.

I would beg those chemists who are interested in this question to kindly compare the above quoted passage of Mr. Baskerville's letter with my condensed note on the subject in the *Proc. Chem. Soc.* (1901, p. 67), in order to decide whether that letter could have had any influence upon the results of my work. It will be seen further from my full paper on this exceedingly difficult subject which will appear in the *Transactions of the Chemical Society*, whether Mr. Baskerville or whether the writer is nearer the truth, and which of us two has the right of claiming priority of the discovery of the complex nature of thorium.—I am, &c.,

Bohuslav Brauner.

Bohemian University, Prague.
October 22, 1901.

* The first facts pointing undoubtedly to the complex nature of thorium were found by me at the beginning of 1896.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 15, October 7, 1901.

Action of Urethane on Pyruvic Acid.—L. J. Simon.—Urethane is condensed by aldehydes, especially in presence of hydrochloric acid, according to the equation—

$$R-CHO+2NH_2-CO_2C_2H_5 = H_2O+R-CH<\begin{matrix}NH-CO_2C_2H_5\\NH+CO_2C_2H_5\end{matrix}.$$

Pyruvic acid combines with urethane directly, without the presence of a condensing agent:—

$$CH_3-CO-CO_2H+2NH_2-CO_2C_2H_5 = H_2O+\begin{matrix}CH_3\\CO_2H\end{matrix}>C<\begin{matrix}NH-CO_2C_2H_5\\NH-CO_2C_2H_5\end{matrix}.$$

The substance formed, diurethane pyruvic acid, can be clearly distinguished from pyruvic acid itself by a number of reactions. It is a white crystalline body, melting at 138—139°. It is non-volatile, but when heated strongly it decomposes, urethane distilling off. It is very soluble in hot or cold alcohol, also in acetone and chloroform, very slightly soluble in cold water, but soluble in hot water, with decomposition into urethane and pyruvic acid.

Bromated Malonic Dialdehyde.—R. Lespieau.—The author fixed hydrobromic acid on to propiolic acid, and obtained a well characterised acid melting at 115°. He tried various experiments with this substance in the attempt to transform it into its isomer, but without success. He then further investigated the groups of atoms, $C_3H_3BrO_2$, and thought that the so-called acid might be the dialdehyde CHO.CHBr.CHO. He experimented on this substance, preparing its potassium derivative and testing its reactions with phenylhydrazine, and finally confirmed his hypothesis. Amongst the accessory products to this reaction he found the acid $CHBr=CBr-CO_2H$, melting at 85°, and also that the dibromated ether, $CHBr=CR-CO_2H$, can be replaced by the alcohol, $CHBr=CH-CH_2OH$, or by its methylic ether. The author has not yet satisfactorily explained the mechanism of these reactions. The formation of a primary aldehydic group by the action of bromine on an alcohol or an ether oxide is normal; that of the secondary group results probably from the intermediate production of a group, $CHBr_2$, due to the following reactions:—

$$CHBr=CH-CH_2OH+Br=CHBr_2-CHBr-CH_2OH,$$

and—

$$CHBr=CBr-CH_2OH+HBr= CHBr_2-CHBr-CH_2OH.$$

Reducing Properties of certain Nitric Ethers.—L. Vignon and F. Gerin.—During a study of oxycellulose one of the authors showed that the nitrocelluloses possess reducing properties. These results have been confirmed

by other chemists. Nitromannite possesses the same reducing properties with regard to cupropotassic solution. The authors now investigate the properties of other nitric ethers to find a repetition of this characteristic. To this end they prepare the nitric derivatives of different mono- and polyatomic alcohols. Their results are shown in the following table.—

Nitric derivatives of:—	Reducing power with regard to cupropotassic solutions.
Methylic alcohol	None.
Ethylic alcohol	None.
Glycol (di)	None.
Glycerin (tri)	None.
Erythrite (tetra)	Slight.
Dulcite (hexa)	Strong.
Mannite (hexa)	Strong.
Mannite (penta)	Strong.

From this table it appears that, starting from those of a certain atomicity, the nitrated derivatives of alcohols possess a special and characteristic reducing power with regard to cupropotassic solution.

MISCELLANEOUS.

Royal Institution.—The Christmas Course of Six Lectures to Young People, at the Royal Institution, will this year be delivered by Professor J. A. Fleming, F.R.S., Professor of Electrical Engineering in University College, London. His subject is "Waves and Ripples in Water, Air, and Æther," and the first lecture will be delivered on Saturday Afternoon, December 28, at Three o'clock. The remaining lectures on December 31, 1901, January 2, 4, 7, and 9, 1902.

The Fermentation of Cellulose.—V. Omeliansky.—The author has isolated and here describes a micro-organism capable of causing the fermentation of cellulose. This bacillus, *Fermentationis cellulosæ*, is anærobic, and belongs to the widely-spread group of butyric ferments. About 70 per cent of the decomposed cellulose is transformed into fatty acids (acetic and butyric), while 30 per cent is transformed into hydrogen and carbonic acid. This fermentation of cellulose differs essentially from the formenic fermentation of the same substance; in fact, in this latter case, it forms only gaseous products—formene and carbonic acid.—*Arch. des Sc. Biol.*, vol. vii., p. 411.

The Oxidation of Hydroxylamine.—G. von Knorre and K. Arndt.—The authors have examined the action of various oxidising agents on hydroxylamine in aqueous solution. The apparatus used in these experiments is fully described in the original paper. It must not be forgotten that the hydrochlorate of hydroxylamine decomposes spontaneously as a result of the prolonged boiling of a solution of this salt. The gaseous products have been analysed by the eudiometric method previously described (*Berichte*, vol. xxxii., p. 2136); the excess of hydroxylamine was estimated by means of permanganate and ferric alum. The oxidising agents used are:—The alkaline nitrates in the presence of hydrochloric or sulphuric acid in variable quantities, hydrate of peroxide of manganese, permanganate of potash, chromosulphuric solution, vanadic acid, sulphate of copper, mercuric chloride, persulphate of ammonium, and peroxide of hydrogen. In nearly every case protoxide of nitrogen is principally formed, with a small quantity of binoxide, while the solution contains variable quantities of nitrous and nitric acids. In the case of vanadic acid alone, nitrogen is chiefly produced, with a small quantity of protoxide. Sulphate of copper gives pure protoxide if the hydroxylamine is in excess. Naturally, permanganate does not give any binoxide of nitrogen.—*Berichte*, xxxiii., pp. 30—42.

The Estimation of Copper in Biological Researches.—Ch. Dhéré.—To detect and estimate copper in organic liquors and tissues, M. Dhéré proposes to operate in the following manner:—The organic matter is destroyed by means of hot sulphuric acid, with the repeated addition of nitric acid to accelerate and complete the combustion. We thus obtain the copper in solution in the form of sulphate of copper. The dilute solution is electrolysed by means of a current of 2 to 5 volts (in the presence of a little nitric acid, which has the property of helping on the electrolysis), which is kept up until a freshly immersed portion of the electrode is no longer coated with copper. The weight of the copper deposited is found by weighing the electrode before and after the electrolysis. We can also estimate the copper by a colorimetric me hod. This is based on the possibility of estimating the amount of copper present in a solution by the intensity of the colouration produced under the action of ferrocyanide of potassium. In the present case the deposited copper is redissolved in nitric acid; the solution is then evaporated *in vacuo* over potash to drive off the whole of the free nitric acid which would otherwise interfere with the coloured reaction; the residue is taken up with water, and a 10 per cent solution of ferrocyanide of potassium added; the intensity of the colour is then estimated by bringing it to the same degree as that of a typical solution prepared with a titrated solution of copper. Under favourable circumstances 1/50th of a milligrm. of copper can be estimated.—*C. R. Soc. de Biol.*, 1900, p. 456.

MEETINGS FOR THE WEEK.

Monday, 4th.—Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. "The Rapid and Approximate Estimation of Free Oxygen in Sewage Effluents and Waters," by Prof. W. Ramsay, F.R.S. "Phthalic Glyceride," by Watson Smith. "Notes on the Manufacture of Varnish by the Pressure Process," by A. J. Smith.

Wednesday, 6th.—Society of Public Analysts, 8. "The Composition of Milk," by H. Droop Richmond, F.I.C. "A Contribution to a Knowledge of the Chemistry of Cider," by Alfred H. Allen, F.I.C. "The Determination of Carbon in Steel by Direct Combustion," by Bertram Blount, F.I.C. "On Enteriditis Sporogenes as Evidence of Sewage Pollution," by M. Dechan.
—— Geological, 8.

Thursday, 7th.—Chemical, 8. "Note on the Non-existence of a Higher Oxide of Hydrogen than the Di-oxide," by W. Ramsay, F.R.S. "The Electrolytic Reduction of Nitrourea," by G. W. F. Holroyd. "The Constitution of Pilocarpine" (III.) and "A New Synthesis of α-Ethyl Tricarballylic Acid," by H. A. D. Jowett. "The Action of Nitric Acid on Methyl Dimethylacetoacetate." by W. H. Perkin, F.R.S. "An Incrustation from the Stone Gallery of St. Paul's Cathedral" and "Note on Asbestos," by E. G. Clayton. "Liquid Nitrogen Peroxide as a Solvent," by P. F. Frankland, F.R.S., and R. C. Farmer.

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THE CHEMICAL NEWS.

Vol. LXXXIV., No. 2189.

SOME RELATIONS BETWEEN PHYSICAL CONSTANTS AND CONSTITUTION IN BENZENOID AMINES.*

Part III.

By W. R. HODGKINSON and L. LIMPACH.

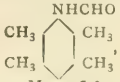
In the *Proc. Chem. Soc.*, 1893, ix., 41, we drew attention to some relationships between melting-points and constitution in some amines, and a further contribution by one of us and Gordan on the same subject appears in the *Trans. Chem. Soc.*, 1901, lxxix., 1080 (see also Chemical News, vol. lxxxiii., p. 297).

Since then, a considerable number of amines, their formyl and acetyl derivatives, have been prepared, it is believed in as pure a state as possible, and their melting-points, &c., determined.

Taking one particular series, the first point noticeable is that the *difference* between the melting-points of the formyl and acetyl derivatives of bases of the same constitution is the same, or very nearly so.

If in any base a methyl group be replaced by ethyl or oxymethyl, the melting-points of their formyl and acetyl compounds are changed. The *differences*, however, appear to be the same as between the formyl and acetyl derivatives of the methyl compounds. For instance, see Table I.

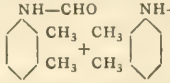
The tetramethyl bases exhibit some other peculiarities. As far as the melting-points of their formyl and acetyl derivatives are indications, they would appear to be built up of two xylidines *less* the melting-point of formanilide, &c. Thus, formyl aminotetramethylbenzenes—

I. 

M. p. 163°.

* Abstract of a Paper read before the British Association (Section B), Glasgow Meeting, 1901.

would *appear* to be composed of twice—

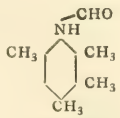
1 : 2-formylxylide – formanilide 

M. p. 104·5° + M. p. 104·5°

= 209°

– 46° (M. p. of formanilide)

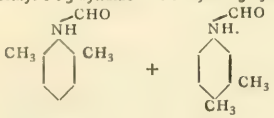
= 163°

II. 

M. p. 183°.

composed of—

Formyl-1 : 5-xylidide + Formyl-2 : 3-xylidide



M. p. 164°. M. p. 65°.

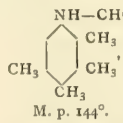
164

65

229

– 46 (M. p. of formanilide)

183

III. 

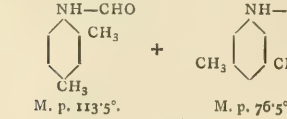
M. p. 144°.

Table I.

	Constitution (*a*).	M.p. formyl compound.	M.p. acetyl compound.	Difference.
Pseudocumidine	$CH_3\ CH_3\ CH_3$ (2 3 5)	121°	164°	43
Ethyldimethyl aminobenzene	$CH_3\ C_2H_5\ CH_3$ (2 3 5)	103°	145°	42
Paraxylidine	$CH_3\ CH_3$ (1 4)	116·5°	139°	22·5
Methyloxymethyl aminobenzene	$OCH_3—CH_3$ (1 4)	86°	109°	23
Cumidine	$CH_3\ CH_3\ CH_3$ (1 2 4)	98°	126°	28
Oxymethyldimethyl aminobenzene	$OCH_3\ CH_3\ CH_3$ (1 2 4)	68°	96°	28

(*a*) For simplicity, the constitution is represented on the plan , &c.

composed of—



113·5
76·5
190·0
– 46 (M. p. of formanilide)
144

ALUMINATE OF MAGNESIUM.

By EM. DUFAU.

The use of the electric furnace enables us to obtain the mono-magnesian aluminate Al_2O_4Mg, or "spinel," with great ease.

The reproduction of this natural compound has been already effected by several chemists, viz., Ebelmen, Daubrée, and Stanislas Meunier, but by the use of more complicated and much longer methods.

An intimate and well-calcined mixture of 200 grms. of alumina and 100 grms. of magnesia is heated in a carbon crucible by means of an arc of 900 ampères and 45 volts. After heating for three minutes, we find in the crucible an entirely crystalline grey mass.

A portion of this mass is pulverised in an iron mortar and treated with hot nitric acid; thus we obtain a colourless crystalline powder mixed with numerous particles of carbon. To effect their separation we take advantage of their different densities, and by putting the powder into iodide of methylene, or into Klein's reagent, we can collect, at the bottom of the liquid, an absolutely homogeneous product which can be immediately submitted to analysis.

The substance is therefore finely powdered and treated in a platinum crucible with sulphate of potassium moistened with sulphuric acid, and then kept at a bright red heat until solution is complete. On cooling, the residue is taken up with water containing hydrochloric acid, and precipitated with a slight excess of ammonia; it is then left on the water-bath for some time, and the separated precipitate is re-dissolved in hydrochloric acid and re-precipitated with ammonia, &c.; this is repeated three or four times. Finally, the aluminium is collected and the magnesia precipitated in the filtrates in the form of ammonio-magnesian phosphate. The following are the figures thus obtained:—

	Found.	Calculated for Al_2O_4Mg.
Al_2O_3	72·72 and 72·43	71·68
MgO	27·43 „ 26·61	28·32

Aluminate of magnesium thus prepared appears in the form of colourless octahedra, it scratches quartz, has a density of 3·57 at 15°, is infusible before the blowpipe, and is only fusible in the electric furnace.

Hydrofluoric, hydrochloric, and sulphuric acids only attack it slowly; nitric acid has no effect. Fluorine has no action in the cold, but attacks it slowly when heated; chlorine, bromine, and iodine have no apparent action. Sulphur, at the temperature of melting glass, has only a very slight action. Carbon does not reduce this aluminate even at the temperature of the electric arc. Finally, however, alkalis in fusion, decompose it with facility, but their carbonates are without effect.

It is very easy to give to this aluminate of magnesium the different colourations shown by the different varieties of spinel; it suffices to add to the reacting oxides 1 or 2 per cent of the oxides of iron, nickel, chromium, or cobalt, &c.; a rose-brown colour has been specially observed on adding oxide of copper.

We have endeavoured to obtain basic aluminates of magnesium, and have heated mixtures of two, three, and four molecules of magnesia for one of alumina, but we have never obtained anything but the mono-magnesian aluminate crystallised in the excess of fused magnesia.—*Bull. Soc. Chim.*, Series 3, vol. xxv., No. 13.

THE UTILISATION OF FLUORIC GASES FORMED IN THE MANUFACTURE OF SUPERPHOSPHATES.

By C. ELSCHNER.

For some years past instructions have been given to inspectors of factories in Germany to prevent the direct escape into the air, from factory chimneys, of the fluoric gases which are given off during the solubilisation of phosphates. In a large number of factories of chemical manures, condensation apparatus by means of water vapour have been installed to retain the fluosilicic acid. Tarred wood chambers have been used with great success; these chambers are from 5 to 6 metres high, 5 to 6 metres long, and from 1 to 5 metres in width, divided into five compartments along their length by means of partitions. These partitions are pierced with holes alternately at the top and bottom, so that the current of gas is forced to traverse the whole length of each compartment. A Körting's apparatus made of hard rubber is placed in each compartment, and throws a fine spray of water in the opposite direction to that of the current of gas. Under the action of the water the fluoride of silicon is decomposed into fluosilicic acid, which is absorbed, and into gelatinous silica. The current of gas, almost entirely purified and freed from its acid constituents, is then allowed to escape up the chimney-shaft. The strongly acid liquor which collects at the bottom of the chambers is drawn into large tanks through leaden pipes. The liquor may then be neutralised with chalk and allowed to run off.

If, however, it is desired to treat these solutions specially it is preferable to keep the more concentrated liquors from the first and second compartments separate from the others; the former titrate up to 10 to 12° B. The liquor from the three other compartments, if too dilute to be of use, can be neutralised with chalk and run off.

To transform the liquor into fluosilicate of soda, it is treated, after filtration by the requisite quantity of a soda salt, such as a 10 per cent solution of sea-salt; it is then allowed to settle, and the precipitate is washed by decantation, passed through a filter-press, and dried. The precipitate can be completely separated and a pure product obtained, by using an excess of chloride of sodium, and constantly stirring the mixture while keeping the temperature at 15—25°.

However, the demand for fluosilicate of soda is not very considerable; it has therefore been found advisable to try and prepare other compounds from the fluorised gases. The fluates of Kessler were first thought of. As is well known, these are solutions of fluosilicate of magnesium and fluosilicate of aluminium, used for the hardening of calcareous stone.

Recently, attention has been drawn to the antiseptic properties of fluosilicic acid, and it has been recommended, amongst other uses, for preserving manures. As a matter of fact this acid appears to be much more efficacious than plaster, superphosphate of lime, or kainite for the preservation of farm-yard manure and for preventing the loss of nitrogen.

In every case the denitrifying action of certain bacteria is checked. On the other hand, however, the increasing

use of aqueous fluosilicic acid is interfered with by reason of the dislike most farmers have to having "bottles of acid" on their premises.

Attempts have been made to absorb the acid by infusorial earth or peat, but these products have not come into vogue.

A patent has recently been taken out for a new preservative for farm-yard manure; it consists of two pulverulent compounds, which have to be used together. One of them is prepared by absorbing as much sulphuric acid as possible by a powdered porous compound; the other is made by incorporating the solution of fluosilicic acid obtained from the first and second compartments of the absorption chambers with ground-up clay. The greater part of the acid combines with the bases contained in the clay. To preserve farm-yard manure one or two handfuls of each powder are strewn over it; by their mixture free fluosilicic acid is given off, and this acts as an antiseptic. This process is certainly an advance; it remains, however, to be seen at what prices these materials can be delivered by the makers. The second of these compounds might be prepared more economically by passing the gases directly over lime, well stirring the mixture, and drying the mass obtained. Instead of sulphuric acid incorporated with a porous body a powdered bisulphate might be employed with advantage. In this manner the antiseptic material would be obtained in a more concentrated form.—*Chemiker Zeitung*, 1900, p. 795.

EXTRACTION OF CYANIDES IN GAS-WORKS.

It is well known that among other impurities coal-gas contains sulphuretted hydrogen, ammonia, and hydrocyanic acid. Washing with water in conjunction with the ammonia in the gas does not suffice to extract this acid in the form of the easily soluble cyanide of ammonium, inasmuch as the carbonic acid, which is always present in the gas in excess, immediately decomposes the cyanide of ammonium formed, into carbonate and hydrocyanic acid. This explains why the ammoniacal waters from gas-works do not contain any cyanide of ammonium.

The small quantity of cyanide retained by these waters occurs in the form of sulphocyanide of ammonium, and a certain amount of cyanogen passes into the purifiers, when the following reaction takes place:—The cyanogen combines with the suboxide of iron, with the small quantity of ammonia still present, and with the sulphur compounds, forming insoluble ferro-cyanides and sulpho-cyanides, which gradually accumulate in the purifiers. Further, the whole of the cyanogen is not even then removed in this manner, but a very appreciable amount can be found in the gas delivered for consumption.

Up to 1880 the contents of the purifiers became a valueless product as far as the gas companies were concerned. The question has now taken, however, quite another aspect since the discovery of so many gold-mines, and the almost universal application, since this time, of the cyanide process of gold extraction. At the present time gas companies are making large profits from the spent contents of their purifiers.

It is, however, nevertheless true that this method of extraction of the cyanides leaves much to be desired. In the first place, the whole of the cyanogen is not recovered; again, it prevents the oxide from being entirely of use in removing the sulphuretted hydrogen; in this way it counteracts the original object of the purifiers.

The process devised by Dr. Bueb, and tried at the gas-works at Dessau, is possessed of great advantages, and deserves special mention, since it removes the whole of the cyanogen before the gas enters the purifiers. The principle is to conduct the gas, after leaving the Pelouze and Audouin condenser, into a special mechanical washer of the "Standard" type, consisting of four or five separate compartments, through which a solution of sulphate of iron flows in the opposite direction to that of the current of gas. In the last compartment the concentrated, freshly-formed solution gives the following reaction in the presence of ammonia and sulphydric acid:—

$$FeSO_4 + H_2S + 2NH_3 = FeS + (NH_4)_2SO_4.$$

Thus the sulphate of iron is transformed into sulphide of iron, and a solution of sulphate of ammonium is also formed. These liquors then pass into the next compartment, and there the ammonia and the cyanogen of the gas form, with the sulphide of iron, an insoluble double salt of cyanide of iron and ammonium, while the sulphuretted hydrogen being again set free is partially carried away with the gas, and partly forms sulphide of ammonium. This reaction continues in the other compartments up to the first where the gas enters, where it terminates.

The liquor, which is black in the first compartment, gradually becomes clearer, and is of a greenish-yellow colour in the last. The product leaves the cyanide washer in the form of a liquid mud, and contains 20 per cent of the yellow prussiate and 6 to 8 per cent of ammonia. This mud is boiled to drive off the ammonia, and passed through a filter-press; this finally gives a cake containing 30 per cent of blue and 44 per cent of yellow prussiate, and it is sold as such; to obtain 100 kilos. of prussian blue it is necessary to use 200 kilos. of sulphate of iron.—*Revue Generale des Sciences*, Year XII., No. 15, August 15, 1901.

SELENOCYANIC COMPOUNDS.

By W. MUTHMANN and E. SCHRÖDER.

Preparation of Selenocyanate of Potassium.—An intimate mixture of 70 grms. of pure KCy with 79 grms. of finely powdered commercial selenium is melted at as low a temperature as possible. Take up with 40 c.c. of water, and heat on the water-bath for three or four hours, renewing the water when necessary; then evaporate to dryness with constant stirring, and take up with 1 litre of boiling absolute alcohol; a current of CO_2 is then passed through the solution for two hours. Filter, drive off the alcohol by distillation, and dry the crystals of KCySe; the return should be from 96 to 98 per cent. In this manner all loss of selenium is avoided.

Preparation of Triselenide of Cyanogen.—Crystals of selenocyanate of potassium are placed in a flat bottomed vessel with one-third to one-half their weight of water, and a current of peroxide of nitrogen gas is passed over the mass, taking care to stir frequently, and to keep the temperature down to 0°. The mass first becomes red, and red crystals are formed having a blue metallic appearance by reflected light; these consist of Cy_3Se_4K, and have been described by Verneuil; they afterwards become yellow, and increase considerably in volume. Towards the middle of the operation it is as well to add, small quantities at a time, of fuming nitric acid; this causes the mass to become very frothy; Cy_2 and HCy are given off. When this reaction is terminated the residue is rapidly drained, then washed with very little water, and finally dried on porous plates in the desiccator. In this manner we obtain a mixture of nitre and triselenide of cyanogen, which is treated with boiling benzene to dissolve the latter. On cooling it is deposited in yellow flakes or needles. The product melts at 132°, forms a deep yellow liquid, and decomposes at 148·5°; when heated in a tube it gives a sublimate of selenium and SeO_2. It is perfectly insoluble in water, but is decomposed by it, forming Se and SeO_2. The best solvents are benzene and chloroform; it is slightly soluble in sulphide of carbon. Analysis and ebullioscopic examination give the formula $C_2N_2Se_3$.

Action of Triselenide of Cyanogen on some Organic Substances.—It has been seen that, in the case of certain bodies, such as CS_2, $CHCl_3$, CCl_4, this action is nil; on the other hand, it has been shown by Verneuil that there is a reaction and a deposit of selenium with alcohol and

ether. The same thing takes place if we rub up some of the triselenide with acetylacetic ether; selenium is deposited, and HCy given off. By distillation at 86—88° under 26 m.m. a yellow liquid with an acid reaction has been extracted; this liquid has a strong garlic odour, and contains selenium but no nitrogen. In the same way there is a reaction with acetone, but this is stopped when the acetone becomes saturated with the HCy produced. —*Berichte*, vol. xxxiii., p. 1765.

THE QUANTITATIVE SEPARATION AND DETERMINATION OF URANIUM.*

By EDWARD F. KERN.

The work described in this article was undertaken with the object of finding out the most accurate and satisfactory method for the technical estimation of uranium.

The usual quantitative methods for the estimation of uranium were first repeated, then new methods for its separation and estimation were tried on solutions containing known amounts of pure salts, and the best conditions for both separation and determination were carefully worked out.

The research was drawn to a close by making a number of assays of uraninite, in which the results obtained from the work on pure salt solutions were applied. These assays tested the methods on the most important ore of uranium, and thus collected the data in the form of analytical methods.

Historical Introduction.

Uranium was discovered by M. H. Klaproth, who separated what he thought to be a new element from pitchblende—also known as uraninite—the principal ore of uranium. This was in 1789, and what he obtained was not the element, but its lower oxide, UO_2. He named the element uranium in remembrance of the planet Uranus, which Herschel discovered in 1781.

From 1789 to 1795 much work was done on the investigation of uranium, but nothing new was discovered till 1840, when E. Péligot succeeded in isolating metallic uranium in powder form by heating uranous chloride (UCl_4) with metallic sodium (*Liebig's Ann. Chem.*, 1842, xli., 141). He made a great number of experiments, the results of which proved that what was previously thought to be the element uranium was its lower oxide (UO_2), which plays the part of a base, a true inorganic radical. This discovery seems to have been an impetus to the further study of this element, as we find records in the different journals, of the years that follow, of several of the eminent chemists of the day investigating uranium, and trying to find new methods for its estimation.

Clemens Zimmerman was the next chemist of note to investigate uranium. He studied methods for isolating the metal, and methods for its estimation and separation from other elements, and prepared many of its salts, studying their chemical and physical properties (*Liebig's Ann. Chem.*, vols. cxix., ccix., ccxiii., and ccxiv.). This work covered a number of years, from 1877 to 1884. So 1877 marks the second revival of interest in the element uranium. The first revival was in 1840, when Péligot isolated metallic uranium. The third revival is the present time, brought on by the great industrial demand for uranium ores.

In 1854 the only use to which uranium was put was for making a very fine black for porcelain painting (Whitney's "Mineral Wealth of the United States"), and from 1850 to 1866 it was much used in photography. At present its uses are (or the preparation of acetate and nitrate salts (which are used as chemical reagents), for the manufacture of a certain highly prized canary-yellow coloured glass, for the preparation of a pigment used for porcelain painting, and, lastly, for making a steel which has properties superior to nickel steel (*Moniteur Industriel*, 1900, xxvii., 44).

Part I.—Separation of Uranium.

Separation of Uranium from Members of the Fifth and Sixth Group.

The only point to be determined for the well-known separation by hydrogen sulphide was the exact acidity of the solution. This was done by mixing standardised solutions of lead, copper, and uranium in different proportions, and precipitating the lead and copper by hydrogen sulphide, under varying conditions of acidity and temperature. The experiments were all conducted quantitatively. These showed that a perfect separation was effected when 1 c.c. of concentrated nitric acid (sp. gr. 1·42) was present to every 50 c.c. of solution, and the solution saturated with hydrogen sulphide in the cold.

With hydrochloric acid, 1 c.c. of concentrated acid (sp. gr. 1·20) to 50 c.c. of solution gave excellent results. This amount must not be exceeded, as when 2·5 per cent of concentrated acid was present the precipitation of the lead was incomplete. Less acid must be present if the precipitation is done from a hot solution, but this is not recommended.

As 5 c.c. of concentrated acid in a bulk of 250 c.c. solution gave a perfect separation of uranium from the metals of the fifth group, whose sulphides are the most soluble —lead and cadmium—and also from copper, these conditions must also be suitable for the other members of this group. Lead requires the least amount of free acid to retain it in solution; then follow in order of succession, cadmium, mercury, bismuth, copper, and silver (Fresenius's "Quantitative Chemical Analysis," 1900, p. 456).

Separation of Vanadium from Uranium.

Vanadium is one of the common associates of uranium, and especially so in the minerals which occur in Colorado. Carnotite, the most common of these minerals, has of late reached commercial importance.

The separation of vanadium from uranium presents very little difficulty unless phosphoric acid is present, in which case the separation is troublesome. Friedel and Cumenge (*Amer. Journ. Sci.*, 1900, x., 135) separated vanadium from uranium by evaporating the solution to dryness with nitric acid. The uranium was then extracted from the dry mass with a warm dilute solution of ammonium nitrate. For this separation, no phosphoric acid should be present as it renders the uranium oxide, with which it is combined, insoluble in the dilute ammonium nitrate solution.

The method for the separation of vanadium from iron by means of mercuric oxide and mercurous nitrate (Blair's "Chemical Analysis of Iron," Third Edition, p. 200), has been used with success by A. C. Langmuir, for the separation of vanadium from uranium in the analysis of carnotite (see Paper read before New York Section of American Chemical Society, at March meeting). The finely divided mineral was dissolved in the smallest possible amount of nitric acid, and the silica filtered off. The solution was diluted to about 500 c.c., and the vanadium precipitated by means of mercurous nitrate as follows:— The nitric acid solution was nearly neutralised with pure yellow mercuric oxide, and the vanadium then precipitated by the addition of a strong solution of mercurous nitrate. The solution was brought to boiling, after which it was filtered. (If chromium, tungsten, or molybdenum are present they go down as mercurous salts with the mercurous vanadate). The precipitate was washed with a warm dilute solution of mercurous nitrate, after which it was dried, ignited, and weighed as V_2O_5. The excess of mercury in the filtrate was removed by means of hydrogen sulphide gas. After expelling the hydrogen sulphide from the filtrate by slow boiling, the uranium was determined by the ordinary method.

* Contribution from the Havemeyer Laboratories of Columbia University. From the *Journal of the American Chemical Society*, xxiii., No. 10.

O. P. Fritchle's Method (*Eng. Min. Journ.*, Nov. 10, 1900; CHEM. NEWS, 1900, lxxxii., 258) is said to be particularly adapted to the mineral carnotite. The finely divided mineral was decomposed at boiling temperature with 10 c.c. nitric acid, taken up with 10 c.c. water, neutralised with a saturated solution of sodium carbonate, added 5 c.c. in excess, and 20 c.c. of a 20 per cent sodium hydroxide solution; it was boiled slowly for half-an-hour, and the precipitate allowed to settle. The vanadium, uranium, and iron were all precipitated by the sodium carbonate, but on adding a moderate excess and a large excess of sodium hydroxide, the vanadium was dissolved while the uranium and iron remained insoluble. Uranium is easily precipitated by sodium carbonate and sodium hydroxide in the presence of an iron salt. The precipitate was washed with a solution of sodium hydroxide. The uranium and iron were then separated by the ordinary method, and each determined volumetrically by means of standard permanganate, after reducing their sulphate solutions at boiling temperature with metallic aluminum.

Separation of Uranium from Members of the Third and Fourth Groups, particularly Iron.

The methods ordinarily used for separating uranium from the other members of the fourth group and those of the third group depends on the solubility of uranium hydroxide and sulphide in an excess of a strong solution of an alkali carbonate. The hydroxides and sulphides of the other members of these two groups are, with the exception of iron and nickel, insoluble in alkali carbonate solutions. The hydroxides of these two metals are only slightly soluble in strong alkali carbonate solutions; in cold dilute solutions they are almost insoluble.

The element which gives the most trouble in effecting a separation from uranium is iron. A great number of methods have been proposed, of which the best known are Pisani's ammonium carbonate (*Comptes Rendus*, lii., 106), and Patera's sodium carbonate methods (*Zeit. Anal. Chem.*, 1866, v., 228), neither of which are very satisfactory. Rose used ammonium carbonate followed by ammonium sulphide (*Zeit. Anal. Chem.*, 1862, i., 410), thus precipitating the iron. This latter method is far from satisfactory, especially if the uranium is small in amount. Rheineck's basic acetate method (CHEM. NEWS, 1871, xxiv., 233) has been used with success when the uranium was present in considerable quantity.

Ether Separation.—The use of ether to effect a separation of iron from uranium was suggested by A. C. Langmuir in a recent article on the analysis of nickel ores (*Journ. Amer. Chem. Soc.*, 1900, xxii., 102). He found that iron could be separated from copper, manganese, aluminum, cobalt, nickel, and zinc, by taking advantage of the solubility of ferric chloride in ether free from alcohol. The chlorides of the other metals are not taken up by the ether, but remain in the aqueous hydrochloric acid solution. When iron is in the ferrous condition, Rothe (CHEM. NEWS, lxvi., 182) found that it was not taken into solution by the ether, but remained with the other metals in the aqueous solution. So it is necessary to oxidise the iron before attempting to make the separation.

Experimental.

The separation of iron from uranium by means of ether was tried, and, as the result, a clean and rather rapid separation has been worked out. This separation depends on the complete extraction of ferric chloride (in an aqueous hydrochloric acid solution) by ether which is free from alcohol, and the retention of uranyl chloride in the aqueous hydrochloric acid solution.

Before undertaking the separation of iron from uranium by means of ether, two solutions containing uranium alone were treated three times with ether, as described in the following experiments, in order to test the solubility of uranyl chloride in ether. These experiments showed uranyl chloride to be entirely insoluble in ethyl ether which is free from alcohol.

The experiments which follow were made with solutions containing both uranium and iron. Measured amounts of a standard uranium nitrate solution and of a standard ferric chloride solution were placed in a small beaker, and the solution twice evaporated to dryness with 10 c.c. hydrochloric acid (sp. gr. 1·20). The dry mass was taken up with about 10 c.c. dilute hydrochloric acid (sp. gr. 1·10), and heated till all salts were dissolved, but not long enough to lose any of the acid by volatilisation. After the solution had cooled, it was poured into a 250 c.c. separatory funnel, and the beaker rinsed out with dilute hydrochloric acid (sp. gr. 1·10). The rinsings were added to the separatory funnel till the volume of the solution had reached 50 c.c. Fifty c.c. of ether, free from alcohol, and previously shaken up with hydrochloric acid (sp. gr. 1·10), were added and agitated for about ten minutes, occasionally relieving the pressure in the funnel. After thoroughly shaking together, the two solutions were allowed to separate, and the lower aqueous hydrochloric acid solution of uranyl chloride, containing some iron, was drawn off, catching it in another separatory funnel. The ether solution of ferric chloride was washed twice with 10 c.c. dilute hydrochloric acid (sp. gr. 1·10), and the washings, after allowing to separate, were run into the funnel containing the uranium.

On determining the amount of iron extracted from the hydrochloric acid solution by the ether, it was found that all the iron was not separated from the uranium by one extraction, about 10·5 per cent of the amount taken remaining in the aqueous solution with the uranium.

On finding that all of the iron was not separated from the uranium by one "ether extraction," two extractions were made on a solution containing 0·1155 grm. uranium, and 0·0901 grm. of iron. The first extraction was made in the same manner as outlined above, and the second as follows:—The solution in the lower separatory funnel was again shaken for about seven minutes with 50 c.c. ether. After thoroughly shaking together, the two solutions were allowed to separate, and the lower aqueous hydrochloric acid layer run into a second funnel. The ether solution was twice washed with 10 c.c. hydrochloric acid (sp. gr. 1·10), and the washings caught in the second funnel. The ether solution was run into a beaker which contained the ether from the first extraction. After distilling off the ether, the iron was determined by titration with 0·01 normal potassium permanganate solution. About 3·5 per cent of the iron taken remained in the aqueous solution with the uranium.

The next five separations of iron from uranium were made by using hydrochloric acid of about 1·10 specific gravity (1 part acid, sp. gr. 1·20, and 1 part distilled water). In all cases three "ether extractions" were made, whereby practically complete separations of iron from uranium were obtained. The solutions contained from 0·0901 to 0·1802 grm. iron, and from 0·0962 to 0·2310 grm. uranium. The amount of metal in their respective solutions was determined volumetrically, and did not vary more than 0·3 per cent of the theoretical amounts taken.

The next five experiments were made by varying the strength of the hydrochloric acid used. The procedure was the same as above, making three extractions with ether. For the first three solutions, hydrochloric acid of about 1·133 specific gravity (2 parts acid, sp. gr. 1·20, and 1 part distilled water) was used; and for the last two solutions hydrochloric acid of about 1·066 specific gravity (1 part acid, sp. gr. 1·20, and 2 parts distilled water). The separation in both cases, of iron from uranium, was incomplete. When hydrochloric acid of 1·133 specific gravity was used the amount of iron remaining with the uranium, after three "ether extractions," was about 6 per cent of the amount taken. With hydrochloric acid of 1·066 specific gravity, the amount of iron which remained with the uranium after three "ether extractions," was about 25 per cent of the amount taken.

The most complete separations of iron from uranium by means of ether are evidently obtained by using hydrochloric acid of 1·10 specific gravity. This is the same

TABLE I.—*Separation of Iron from Uranium by Extraction with Ether.*

Expt. No.	Specific gravity of HCl used.	Volume of sol. at first extraction. C.c.	Number of ether extractions made.	Ether used for— First extract'n. C.c.	Second extract'n. C.c.	Third extract'n. C.c.	Theoretical amount of uranium taken.	Amount of uranium determined in aqueous HCl solution.	Theoretical amount of iron taken.	Amount of iron determined in ethereal extract.
1.	1·10	40	3	50	40	40	0·09625	0·09588	—	—
2.	1·133	40	3	50	40	40	0·09625	0·09643	—	—
3.	1·10	50	1	50	—	—	0·11550	0·13171	0·09010	0·08415
4.	1·10	50	1	50	—	—	0·11550	0·14700	0·09010	0·07700
5.	1·10	50	2	50	50	—	0·11550	0·12466	0·09010	0·08690
6.	1·10	40	3	50	50	50	0·09625	0·09643	0·09010	0·08993
7.	1·10	25	3	75	50	35	0·11550	0·11525	0·09010	0·09020
8.	1·10	25	3	75	50	35	0·09625	0·09643	0·18021	0·18029
9.	1·10	25	3	75	50	35	0·19250	0·19228	0·09010	0 08993
10.	1·10	25	3	75	50	35	0·23099	0·23069	0·09010	0·09037
11.	1·133	40	3	50	50	50	0·09625	0·10584	0·09010	0·08663
12.	1·133	25	3	75	50	35	0·11550	0·12068	0·09010	0·08580
13.	1·133	25	3	75	50	35	0·19250	0·20815	0·09010	0·08250
14.	1·066	25	3	75	50	35	0·09625	0·20933	0·18022	0·12705
15.	1·066	25	3	75	50	35	0·23099	0·27224	0·09010	0·07150

strength as was found by Speller (CHEM. NEWS, 1901, lxxxiii., 124) to be the best for the separation of iron from copper, manganese, aluminum, chromium, cobalt, and nickel.

When rather concentrated hydrochloric acid (sp. gr. 1·133) was used for the solution of the chlorides of iron and uranium, it was noticed that on diluting the aqueous solution, after agitating with ether, quite an amount of ether separated. This seems to explain the reason why iron is not readily separated from uranium by means of ether when strong hydrochloric acid is used to bring their chlorides into solution, the iron being retained by the large quantity of ether which remains with the acid solution.

The results obtained are shown in Table I.

Separation of Uranium from Cobalt, Nickel, and Zinc.

Wolcott Gibbs separated uranium from cobalt, nickel, and zinc by means of hydrogen sulphide. He states that this method is much simpler than those ordinarily used, and also gave excellent results (Silliman's *Amer. Journ. Sci. and Arts*, 1865, [2], xxxix., 62). To the neutral or nearly neutral solution of the chlorides of uranium, cobalt, nickel, and zinc, add sodium acetate in excess, and a few drops of acetic acid. The solution is boiled, and a rapid current of hydrogen sulphide passed through the boiling solution for half-an-hour. Every trace of the cobalt, nickel, and zinc is precipitated as sulphides, while the whole of the uranium, and any manganese, if present, remains in the boiling solution. The precipitate is thrown on a ribbed filter, and quickly washed with cold hydrogen sulphide water. The precipitate is easily washed, and though the sulphides of cobalt and nickel formed in this manner are more easily oxidised than when precipitated by sodium sulphide from a boiling solution, they will be found to present no difficulty as regards oxidation upon the filter. If manganese is in the filtrate it may be determined by boiling with hydrochloric acid, and precipitating it in the usual manner with sodium carbonate. The uranium in the filtrate is determined by the ordinary method.

Rose separated uranium from cobalt, nickel, and zinc by means of barium carbonate (Rose's "Chimie Analytique—Analyse Quantitative," 1862, p. 248). The precipitation of the uranium is complete from uranic solutions which contain a small amount of free acid, either hydrochloric or nitric acid. Barium carbonate, which is diffused in water, is added in excess, and the solution allowed to stand twenty-four hours. The presence of ammonium chloride is necessary in order to keep the cobalt, nickel, and zinc in solution. The uranium is separated from the excess of barium carbonate by dissolving the precipitate in hydrochloric acid, and adding dilute sulphuric acid. The uranium in the filtrate is precipitated with ammonia, and weighed as oxide. C. Rammelsberg (*Chem. Centrabl.*, 1884, p. 806) employed this method to separate uranium from cobalt and nickel, and obtained excellent results; but when manganese and zinc are present it cannot be advantageously employed.

(To be continued).

A NEW SOLUTION FOR THE COPPER VOLTAMETER.

By WILLIAM K. SHEPARD.

THE importance of the convenient and accurate method of measuring electric currents by the voltameter depends very largely upon the construction of a voltameter which admits of high current densities.

The silver voltameter gives results of a high degree of accuracy, but is not conveniently used except for small currents; the copper voltameter, however, from the cheapness of its materials, finds employment in the laboratory for the measurement of comparatively large currents.

As ordinarily used, the copper voltameter is subject to irregularities due to the solvent effect of the solution in some cases and the oxidation of the copper in others. The voltameter solution recently investigated by the writer commends itself by the facts that these irregularities are avoided, and that approximately twice the current density permissible with solutions hitherto in use may be employed without loss of accuracy, thus allowing large currents to be measured without inconveniently increasing the size of the electrolytic cell.

Many different solutions for the voltameter have been recommended by various experimenters. Gray (*Phil. Mag.*, 1886, xxii., p. 289), using a copper sulphate solution of density 1·15 to 1·18 with 1 per cent free sulphuric acid, found that the highest current density desirable was 0·02 ampère per square centimetre of cathode surface.

Vanni (*Wied. Ann.*, 1891, x., p. 214; and *Phil. Mag.*, 1888, xxv., p. 179) observed that a copper sulphate solution of density 1·12 with 1 per cent free sulphuric acid dissolved copper, and therefore gave indications always too small. With an increase of the current density the deduced electro-chemical equivalent of the copper increased. A solution neutralised with copper hydrate, on the contrary, yielded results in constant excess, probably on account of the oxidation of the copper. By adding to a litre of the normal solution $\frac{1}{2}$ grm. of a solution which contained 1 per cent sulphuric acid, he found neither a gain nor a loss in the weight of a piece of copper immersed in it. With this solution he successfully used a current density of 0·011 $\frac{\text{ampere}}{\text{c.m.}^2}$, but no experiments seem to have been made to determine the limit.

Œttel (*Chemische Zeitung*, 1893, p. 543) obtained smaller deposits of copper from copper sulphate solutions than Faraday's law demands resulting from the formation of oxygen compounds, such as HSO_4. By the addition of alcohol, these losses were avoided. He advised as the best solution :—

150 grms.	$CuSO_4$
50	,,	H_2SO_4
50	,,	Alcohol
1000	,,	H_2O

Beach (*Am. Journ. Sci.*, 1893, xlvi., p. 81) investigated the use of copper nitrate in the voltameter. His solution, after neutralisation, had a density of about 1·53, and contained one drop of a saturated solution of NH_4Cl to 100 c.c. of the nitrate. The NH_4Cl was added to prevent the oxidation and consequent excess of deposit which occurs when a neutral solution is used alone. He found that he could use a much higher current density with this solution than with the copper sulphate solutions commonly used. But as copper nitrate is relatively expensive in comparison with the sulphate, it is not so well suited for general laboratory use.

It seemed to the writer of interest to attempt the use of a neutral solution of the sulphate in the same manner, with the aim of increasing the allowable current density. The solution was prepared as follows :—A saturated solution of copper sulphate was boiled for a short time to expel the air, and then kept at 100° C. for about an hour in contact with metallic copper in order to neutralise the solution; the density was then about 1·20. A very small amount of NH_4Cl was added, about 0·05 of 1 per cent.

Two voltameters were used in the investigation. They were connected in series in order to see how the different solutions would agree when using exactly the same current. Each voltameter consisted of three anode and two cathode plates, the cathode plates being placed alternately between the anodes at distances of about 2 c.m. The plates were 10·5 × 19 c.m., of which a working cathode surface of about 600 $c.m.^2$ was employed. The voltameters were used in battery jars 20 c.m. high and 15 c.m. in diameter.

The method used in the preparation of the cathode plates was that given by Gray (*Phil. Mag.*, 1886, xxii.). The edges and corners were well rounded and the plates polished with sand-paper. They were next placed in water slightly acidulated with sulphuric acid for a short time to remove any trace of oxide, rinsed in clean water, dried with filter-paper and then over a gas flame. After copper had been deposited, the plates were not exposed to the air for a time longer than absolutely necessary before the copper sulphate solution had been completely washed off. The reason for this is that a copper plate oxidises rapidly when wet with a solution of neutral copper sulphate and exposed to the air. This was accomplished by removing the voltameter plates as a whole from the solution and dipping at once into water containing a few drops of sulphuric acid. They were then rinsed in clean water, dried with filter-paper and over a flame.

Gray's solution was first tried for comparison. Very good deposits were obtained using a current density up to about 0·03 $\frac{\text{ampère}}{\text{c.m.}^2}$; but the deposits would sometimes differ as much as 1 per cent in the two voltameters.

Œttel's solution gave fine deposits for low current densities. When, however, the current density was increased, the plates blackened badly, and copper was found in the form of powder on the bottom of the jars. The highest current density permissible with this solution was 0·02 $\frac{\text{ampère}}{\text{c.m.}^2}$.

Then the solution with NH_4Cl, prepared as above, was investigated in the same manner, For low current densities, it gave as good results as had been obtained with either Gray's or Œttel's solution, but, in contradistinction to these, the results continued to be satisfactory when these limits were widely surpassed. With a current of 20 ampères the density was increased, by raising the plates so as to lessen the immersed surfaces, to a value even more than 0·05 $\frac{\text{ampère}}{\text{c.m.}^2}$. Notwithstanding this very material increase in the demands upon the voltameter, the deposits still remained perfectly satisfactory. With 30 ampères and a current density of 0·045 $\frac{\text{ampère}}{\text{c.m.}^2}$ the solution still gave results differing by less than 1 per cent.

The voltameters were then filled, one with Gray's or Œttel's solution, and the other with the new solution. When employed for low current densities, the solutions in all cases gave deposits agreeing within the limits of error imposed by the methods employed.

With regard to the constancy of the apparent electrochemical equivalent when a high current density was used with this solution, no exact statement can be made, as the absolute measurement of the current was not attempted. In the first part of this investigation a Weston ampèremeter was included in the circuit, the error of which the writer has reason to believe was less than 1 per cent. Assuming the indications of this instrument to give the true values of the current, the electro-chemical equivalent obtained from the new solution was fairly constant.

The results are not given, as different values of the current being used they included the errors of the instrument.

Having now performed these preliminary experiments showing that the solution could be employed for large current densities without loss of accuracy, and having obtained a fair idea of the working of the solution, experiments were begun with the aim of eliminating the error of the instrument.

Another Weston ampèremeter was obtained which read only to 15 ampères, each ampère division being divided into ten parts. So that with this instrument the current could be measured with an error in the reading of less than one-fiftieth of an ampère. The instrument was not assumed to be correct, but after the experiments had been finished the results were averaged, and, taking the electrochemical equivalent of copper to be 0·000329 $\frac{\text{grm.}}{\text{ampère sec.}}$, the true value of the current at the division used on the instrument was obtained.

Only one point on the ampèremeter was used, namely, the one which gave the nearest value to 15 ampères. Thus, with the same division and changing the current density by raising the immersed surfaces of the voltameter plates, the error of the instrument was eliminated.

From what has just been said, it will be plain that the results given below are not presented as determinations of the electro-chemical equivalent of copper; the experimental data are reduced to that form simply for convenience in comparing them.

The current was obtained from a storage battery of 50 cells, and was kept constant by means of a copper sulphate resistance which could be varied at will by varying the distance between the copper plates.

An auxiliary circuit was arranged whose resistance was equal to that of the two voltameters. The current was thrown by means of a switch first through the auxiliary circuit to the ampèremeter and resistances included in the circuit. These were allowed to heat up until everything became constant, and the resistance adjusted so as to give the desired reading of the ampèremeter. Then the current was thrown through the voltameters, and assumed the desired value instantly.

The duration of an experiment was twenty minutes, so that a deposit of about 6 grms. was obtained. This deposit showed no oxidation, even up to the highest current density used, which was greater than 0·07 $\frac{\text{ampere}}{\text{c.m.}^2}$.

The results are arranged in series according to their respective current densities, as follows :—

Series I.

Current Density = 0·02 $\frac{\text{ampère}}{\text{c.m.}^2}$.

No.	Equivalent × 10⁷.
1.	3287·2
2.	3295·0
3.	3288·4
4.	3288·9
5.	3292·8
6.	3297·2
7.	3286·8
8.	3288·4
9.	3293·9
10.	3289·4
11.	3287·2
12.	3293·4

The mean of these values is 3290·7, with a probable error of ± 2·4 for a single observation.

Series II.

Current Density = 0·03 $\frac{\text{ampère}}{\text{c.m.}^2}$.

No.	Equivalent × 10⁷.
1.	3288·4
2.	3291·7
3.	3296·7
4.	3291·7
5.	3292·8
6.	3288·3
7.	3295·5
8.	3295·9
9.	3294·4
10.	3287·2
11.	3288·4
12.	3288·9

The mean of these values is 3291·7, with a probable error of ± 2·3 for a single observation.

Series III.

Current Density 0·04 $\frac{\text{ampère}}{\text{c.m.}^2}$.

No.	Equivalent × 10⁷.
1.	3287·8
2.	3294·4
3.	3287·2
4.	3284·5
5.	3283·9
6.	3283·4
7.	3296·7
8.	3295·0
9.	3292·2
10.	3295·5
11.	3296·1
12.	3296·7

The mean of these values is 3291·1, with a probable error of ± 3·6 for a single observation.

Series IV.

Current Density 0·05 $\frac{\text{ampère}}{\text{c.m.}^2}$.

No.	Equivalent × 10⁷.
1.	3286·2
2.	3286·2
3.	3290·5
4.	3293·4
5.	3288·4
6.	3286·8
7.	3297·2
8.	3292·8
9.	3285·5
10.	3287·2
11.	3286·8
12.	3293·4

The mean of this series is 3289·5, with a probable error of ± 2·6 for a single observation.

Series V.

Current Density 0·06 $\frac{\text{ampère}}{\text{c.m.}^2}$.

No.	Equivalent × 10⁷.
1.	3288·4
2.	3294·4
3.	3287·2
4.	3290·0
5.	3292·8
6.	3290·5
7.	3291·7
8.	3295·0
9.	3283·9
10.	3287·2
11.	3287·2
12.	3291·1

The mean of these values is 3290·0, with a probable error of ± 2·2 for a single observation.

Series VI.

Current Density 0·07 $\frac{\text{ampère}}{\text{c.m.}^2}$.

No.	Equivalent × 10⁷
1.	3291·7
2.	3288·9
3.	3291·1
4.	3286·2
5.	3290·5
6.	3290·0
7.	3287·2
8.	3286·2
9.	3290·5
10.	3292·8
11.	3286·2
12.	3282·8
13.	3291·7
14.	3287·2
15.	3292·2
16.	3288·9

The mean of these values is 3289·0, with a probable error of ± 1·9 for a single observation.

The results are arranged for comparison in the following table :—

Series.	Current density.	Mean.	Probable error of mean.
I.	0·02	3290·7	±0·7
II.	0·03	3291·7	±0·7
III.	0·04	3291·1	±1·0
IV.	0·05	3289·5	±0·7
V.	0·06	3290·0	±0·6
VI.	0·07	3289·0	±0·6

These results show no dependence upon the current density. In fact, series VI., which differs most from the others, could be slightly increased for the following reason. The day after this series was taken the watch which had been used to measure the time was rated with a clock and found to be gaining at the rate of two seconds an hour when lying at the side of the ampère-meter. This was doubtless caused by the magnetic field of the ampère-meter, as the watch at other times was very correct.

If a connection were applied for this to series IV. it would increase it by about one part in 1800, so that it would become 3290·6, which is in still closer agreement. During series III., IV., V., which were taken after this fact had been discovered, the watch was rated and proper connections were applied. But as the watch had not been rated during series I., II., and VI., the corrections cannot be applied to them.

It is also proper to observe that although the current density was widely varied there is no loss of accuracy, as is shown by the probable errors of a single observation in the different series.

For current densities of 0·05 $\frac{\text{ampère}}{\text{c.m.}^2}$ or greater the solution was found to heat a little during the first experiment. Results which were obtained during the rise in temperature of the solution were always slightly greater than those obtained after the solution had become warm and at a uniform temperature throughout. The unequal temperature of the solution may be avoided by stirring or by making a preliminary experiment to warm up the solution. The best way was found to heat the solution by means of a flame to a temperature of about 35 or 40° C. before making an experiment. The deposits were then found to be very satisfactory even up to a current density of over 0·07 $\frac{\text{ampère}}{\text{c.m.}^2}$ and the resulting values of the equivalent to agree closely with those obtained with the low current densities.

The results given in series III., IV., V., and VI. were obtained with the solution at a temperature from 35 to 40° C., while series I. and II. were obtained with the solution at the temperature of the room, about 20° C. We see therefore that the temperature from 20° to 40° C. has practically no influence upon the results given by the solution; but that any *inequality* in the temperature of the solution will cause slight errors, and therefore should be carefully avoided.

The same solution was used throughout the second part of this investigation. Perhaps fresh solutions would have given more consistent results, but certainly no large error is introduced by the repeated use of the solution.

We may collect the results with this solution as follows:—

The weight of copper deposited is practically independent of the temperature between 20° and 40° C.

The results are independent of the current density within the limits given.

The solution may be used a large number of times.

The solution may be used with a current density two or three times as great as that permissible with others commonly in use, so that to measure a given current a considerable smaller voltameter may be employed than with the older solutions.

Current-measuring instruments may be calibrated by its means with an error of only about one-tenth of one per cent.—*American Journal of Science*, [4], xii., No. 67.

NOTICES OF BOOKS.

Elementary Experimental Chemistry, Inorganic. Completely Illustrated with Full-page Engravings of all the Apparatus and Chemicals used in Experiments. For Students in High Schools and Junior Classes in Colleges, and Private Learners. By W. F. Watson. New York: A. S. Barnes and Co. London: Gay and Bird, 22, Bedford Street, Strand. 1901. Pp. xviii.—320. Illustrated.

This volume has a pleasant appearance, and a closer examination shows it to be excellently adapted to the purposes for which it has been written. As stated in the preface, this text-book aims "to present the fundamental principles of elementary chemistry in a brief, clear, and logical manner, illustrating all important points as far as consistent by appropriate experiments."

The author recognises the fact that there are two classes of students who take an elementary course in chemistry, those intending to pursue the science by more extended studies, and those who complete their study in a single course; the latter is by far the larger class, and for them this book is admirable in many respects.

The subject is treated in a straightforward, commonsense way, with no peculiar fads incorporated, and the work is written in good strong English, easily comprehended by beginners, and avoiding childish expressions (supposed to be more easily understood) that will have to be dropped as the student advances.

The text is interspersed with no less than two hundred experiments, the directions for making which are clearly given without waste of words.

One peculiar, and as the reviewer thinks unwise, arrangement of matter must be noted; the important subject of *combustion* is first reached in Chapter XXXIV., after an elementary chapter on "Organic Compounds," and 88 pages further on in the book than the chapter on the "Atmosphere." Yet the two hundred and sixty pages preceding treat of phenomena and operations in which oxidation frequently plays an important part; it seems to the reviewer that Chapter XXXIV. might better follow Chapter XXIV.

As set forth on the title-page, one of the features of the book is the method of illustration. Twenty full-page reproductions of well-made photographs exhibit every piece of apparatus and every substance used in the experiments. These plates are artistically excellent, but fail in an important respect (easily remedied in a second edition) to accomplish their object. They are not accompanied by explanatory notes, and there is no reference to the individual apparatus in the text. Plate IV., for example, exhibits no less than six large apparatuses interspersed with sixteen or more bottles, dishes, &c., and the beginner finds no means to identify the special apparatus for generating hydrogen sulphide, or to distinguish it from the Woulfe apparatus for generating hydrogen chloride. If each figure on the plate bore a letter or number, and each plate was accompanied by a key, the use of the apparatuses might be clearly indicated. One extra page following each plate could be introduced in a second edition.

The Appendix contains a useful list of "Common Chemical Synonyms and Colloquial Terms," with their scientific equivalents; and many valuable tables of contents compactly printed.

Teachers of elementary classes will do well to give this book a thorough trial. H. C. B.

Researches on Cellulose, 1895—1900. By C. F. Cross and E. J. Bevan. London, New York, and Bombay: Longmans, Green, and Co. 1901. Pp. 180.

There is a good deal of confusion attaching to the use of the word "cellulose"; this is due to various causes, one of which is the curious specialisation of the term in Germany as the limited equivalent of "wood-cellulose." Another influence which the authors consider prevents the recognition of the obvious classification of the "celluloses" is the empiricism of the methods of agricultural chemistry. Physiologists, again, have their own views and methods in dealing with cellulose, and have had hitherto but little regard to the work of the chemist in differentiating and classifying the celluloses on a systematic basis.

After the Introduction, which deals with the general outline of the subject, and the criticisms which were written on the book entitled "Cellulose," published in 1895, the volume is divided into eight sections according to the table of contents, though in the letterpress there is little or nothing to indicate where one section ends and another begins; however, these sections comprise the general chemistry of the typical cotton cellulose, with a table giving the relative values of five methods of estimating the yield of "end-product" or cellulose; the final conclusion being that none of the processes fulfil the requirements of an ideal method. Schulze's method appears to give the nearest approximation to the "actual cellulose" of the raw material. Other sections deal with such matters as the decompositions of cellulose, such as throw light on the problem of its constitution; furfuroids, *i.e.*, pentosanes and furfural-yielding constituents generally, the lignocelluloses, and the pectic group.

From the point of view of the chemist there has been a

very large development of the cellulose industries during the last five years, and this development is principally marked by the success of the newer ones; among these may be mentioned the treatment of the "roving" in the spinning frame, in flax-spinning, by the addition of reagents to the macerating liquid; the alkaline salts used are chiefly sulphite and phosphate of soda. There is a steady growth in the consumption of wood-pulps (cellulose). In regard to the paper trade of the world, this continues to be one of the most prominent characteristics of its evolution. There have been no important developments in the purely chemical processes involved in the several systems of preparing cellulose from wood. The acid methods (bisulphite processes) have developed much more extensively than the alkaline, the latter including the caustic soda and the mixed sulphide (Dahl) process.

The book is printed on Standard Printing Paper, made to the specification of the Society of Arts Committee (see page 160), and is supplied with two indices, one of subject-matter, the other of author's names.

Handbook on Petroleum for Inspectors under the Petroleum Acts. By Captain J. H. Thomson and Boverton Redwood. London: Charles Griffin and Co. 1901. Pp. 298.

Besides being of practical utility to officers of local authorities under the Petroleum Acts this volume is intended, as indicated by its sub-title, "for those engaged in the storage, transport, distribution, and industrial use of petroleum and its products, and calcium carbide, with suggestions on the construction and use of mineral-oil lamps."

It is well known, the authors tell us, that only a small proportion of the petroleum used in this country is under direct control through the operation of the Petroleum Acts, but it is not a matter of equally common knowledge that arrangements, more or less adequate, are usually adopted to provide for the safe storage of such petroleum as is not under direct legal control.

In the present volume, which consists of eleven chapters and sixteen appendices, only such particulars of the geographical and geological occurrence of petroleum, and of its production and refining, are given as to afford an intelligent appreciation of the subject. The real object of the book is concerned with the safe storage, transport, &c., of petroleum.

One of the most important points in connection with the safe storage of petroleum is what is called "flash-point"; the broad principle on which such tests are carried out are as follows:—A sample of the oil to be tested is gradually heated up in a small vessel until, on the application of a light, a blue flame or flash is seen in the space above the surface of the liquid. The temperature of the oil is noted, and this temperature is commonly called the "flash-point" of the oil. This point, however, varies very considerably according to the conditions under which the tests are carried out, and to speak of the flash-point without giving the method by which it was arrived at is as meaningless as to mention a degree of temperature without saying whether Fahrenheit or Centigrade is meant.

Another method of testing petroleum consists in determining the temperature at which the oil takes fire and continues to burn when a light is applied to the surface; this is called the "fire test" of the oil, but though in use in several of the American States, it has never been adopted in this country except for lubricating oils. In Chapter VI. a large amount of information is given on this subject; in fact, we consider this chapter to be one of the most, if not the most, important in the book.

Chapters VII. and VIII. deal with the historical and legislative side of the question, while in Chapter IX. the precautions necessary with petroleum are fully given.

Chapter X. on petroleum oil-lamps is another important one, and contains much valuable information, both on the choice of a lamp and their management. In this connection we think it as well to quote the following passage:—"It is not too much to say that 90 per cent of the accidents which have occurred, whether by explosion of a lamp or otherwise, have been directly due to gross carelessness, ignorance, or the use of lamps after they have become dirty or broken, or defective; these cases being aided by the mistaken economy which induces persons to buy cheap and flimsy lamps rather than those of safer and at the same time more durable construction."

The Appendices contain a good deal of miscellaneous information, though chiefly of a legislative kind; while the whole work cannot fail to be of great value to those for whose use it was written.

Coal-tar and Ammonia. By George Lunge, Ph.D. Third and Enlarged Edition. London: Gurney and Jackson. Pp. 929.

The growing importance and value of this work is well shown by its rapid increase in size since the first edition. That edition, which was published in 1882, consisted of 383 pages of letterpress and 88 diagrams; the second edition, published in 1887, contained 739 pages and 191 diagrams. This second edition having become exhausted, a third has been prepared consisting of 929 pages, and containing 285 diagrams.

The volume is divided into fifteen chapters, beginning with destructive distillation and the production and application of tar.

The production of coal-tar at the gas-works, tar and ammonia as by-products in coke-making, from gas producers and from blast-furnaces, and the properties of coal-tar and its constituents, are dealt with in Chapters II. and III. Chapter V. begins with some historical notes on the distillation of coal-tar; this was first carried out by Henry Hawkins in 1746, half a century before the first introduction of gas lighting, and a patent was granted to him on the 7th of August of that year; the principles of distillation appear quite clearly in this old patent. In succeeding chapters, VI. to X., the author goes fully into the production, properties, utilisation, &c., of pitch, anthracene oil, creosote oil, carbolic acid and naphthalene, light oil, and crude naphtha.

In Chapter XI. the rectification by steam is gone into, with a full description of ordinary and special steam-stills; the final products are also here fully described, and their applications discussed.

Chapters XII. to XV. deal entirely with ammonia, such as the sources from which it is obtained, the composition and analysis of ammoniacal liquor, and the properties of its constituents, the working up of ammoniacal liquors, and other technically important ammonium salts. This volume has been compiled with great care, and is thoroughly up to date; both the table of contents and the index are full and comprehensive.

Practical Organic Chemistry for Advanced Students. By Julius B. Cohen, Ph.D. London: Macmillan and Co. New York: The Macmillan Company. Pp. 284.

The present volume is an enlargement of the one published in 1887, and has been completely re-written.

The chief additions are the introductory chapters on organic analysis and molecular weight determinations, and an extension of the appendix. Great skill is required in the manipulative part of organic chemistry, and success can only be achieved by constant practice and close attention to the rules and instructions given.

These instructions are set out with great clearness by the author, and will doubtless be of considerable value to the student.

The first forty-one pages briefly describe the methods of organic analysis; that is, the estimation of carbon, hydrogen, nitrogen, sulphur, and the halogens; also the determination of molecular weights by (1) the vapour-

density method, (2) the cryoscopic or freezing-point method, and (3) the boiling-point method. The remainder of the book is devoted principally to the preparation of the more familiar organic bodies; the materials required for the preparation are first given, then the method of procedure is minutely described; this is followed by equations and formulæ illustrating the reactions, and, finally, the properties of the body formed are given. The book is very clearly written, and well indexed.

Laboratory Companion for use with Shenstone's Inorganic Chemistry. By W. A. Shenstone, F.R.S. London: Edward Arnold. 1901. Pp. 117.

This book consists of a reprint of most of the experiments in Part I. of the author's "Inorganic Chemistry," together with a few other experiments and a number of exercises. It is intended merely as a laboratory companion, principally to save the larger work from being spoilt by the accidents which are inevitable with young beginners. The experiments are only qualitative, but are clearly though in many cases briefly described. If properly used the book will be of great assistance both to the teacher and his pupils.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 16, October 14, 1901.

New Series of Experiments Relative to the Action of Hydrogen Peroxide on Silver Oxide.—M. Berthelot.—The investigation of the reaction of hydrogen peroxide on silver oxide having given rise to much discussion, the author undertakes a new series of experiments, which seem to remove all doubt as to the formation of particular silver peroxides. These experiments establish, by rigorous comparative measurements, that the peroxide of silver formed during the first stages of the reaction behaves with regard to dilute acids in a perfectly different manner from ordinary silver oxide, with which formerly it was confused. During the course of this investigation he obtains numerical values for all constants by means of the calorimeter and chromometer, such as:—Heats evolved, gaseous volumes, composition by weight of the products obtained, and time occupied in the transformations. All these were formerly taken separately, and are now verified for the fourth time, after twenty years. In fact, this time the author repeats all the operations in a continuous series of precise measurements, executed without interruption, in a special vessel and without the intervention of other manipulations or auxiliary agents. The results of the experiments are given in various tables.

The Inversion-points of Dilution.—Albert Colson.—The specific heat of a solution is not the mean of the specific heats of its constituents. From this fact, it results that the heat of solution and the heat of combination are variable up to a definite point, at which point certain heats of solution change in sign at a definite temperature. M. Berthelot established the point of inversion from the specific heats, and controlled these calculations by direct experiments made on solutions of sodium sulphate and potassium carbonate. The author now investigates saline solutions at temperatures near 100°. He verifies M. Berthelot's experiments, and also he establishes the existence of a temperature at which the heat of dilution of any solution whatsoever of a salt is zero, and at which no physical or chemical change takes place. His experiments are carried out on an aqueous solution of marine salt, and a curve is drawn and described to illustrate the changes.

Action of Urea on Pyruvic Acid. Homoallantoic Acid and Pyruvile.—L. J. Simon.—The action of pyruvic acid and urea takes place in two phases. In the first, an acid compound is formed, to which the author gives the name homoallantoic acid,—

$$CH_3—CO—CO_2H + 2NH_2—CO—NH_2 = H_2O + \begin{matrix} CH_3 \\ CO_2H \end{matrix} > C < \begin{matrix} NH—CO—NH_2 \\ NH—CO—NH_2 \end{matrix}.$$

In the second phase, internal dehydration takes place between the carboxyl and one of the amine groups, with formation of pyruvile,—

$$\begin{matrix} CH_3—C—CO_2H \\ NH_2—CO—NH \diagup \quad \diagdown NH—CO—NH_2 \end{matrix} = H_2O + \begin{matrix} CH_3 \\ NH_2—CO—NH \end{matrix} > C \begin{matrix} \text{———} \\ \diagdown \end{matrix} \begin{matrix} \text{———} CO \\ \diagup \quad | \\ NH—CO—NH \end{matrix}.$$

By slightly modifying the conditions of the reaction, the author succeeds in isolating the intermediate body. It is highly probable that allantoic acid is obtained in the same manner, starting from glyoxylic acid. The reaction is similar to that already described for urethane. The action of water on homoallantoic acid is also examined.

Nitric Derivatives of Pentaerythrite.—Leo Vignon and F. Gerin.—The authors deduce from their experiments the following two conclusions:—1. That the nitrated derivatives of those alcohols having an open chain whose atomicity is equal to or greater than 4 manifest reducing properties with regard to cupro-potassic solution. For example, the tetranitrated derivative of erythrite, $(NO_3)CH_2—CH(NO_3)—CH(NO_3)—CH_2(NO_3)$, the nitrated derivatives of dulcite (hexa), and of mannite (penta and hexa) exhibit this reducing property, whilst the nitrated derivatives of methylic and ethylic alcohols, glycol, and glycerin do not. 2. That the tetranitrated derivatives of pentaerythrite,—

$$\begin{matrix} CH_2—NO_3 \\ | \\ NO_3—CH_2—C—CH_2—NO_3, \\ | \\ CH_2—NO_3 \end{matrix}$$

are void of all reducing power. It seems necessary, then, to admit that certain nitric ethers have a special constitution, and the authors intend to investigate this matter further.

Bulletin de la Société Chimique de Paris. Series 3, Vol. xxv., No. 11.

Contribution to the Study of Indium.—C. Chabrié and E. Rengade.—Already noticed.

A Molecular Combination formed by Iodide of Methyl and Methylic Alcohol.—J. Meunier.—While rectifying the product of the preparation of iodide of methyl by means of methylic alcohol, iodine, and phosphorus, without having previously removed the excess of methylic alcohol by washing with water, the author obtained a liquid boiling at 37·3° under 747 m.m., and at 37·9° under 760 m.m. This liquid is colourless, and resembles iodide of methyl when freshly distilled, but when exposed to diffused light it rapidly becomes coloured, and after a few days it has a decidedly brown appearance. It does not even remain colourless in the dark. The remarkable constancy of its boiling-point, and the fact of its composition answering to a definite formula, is sufficient to cause us to regard it as a definite compound; it has also another characteristic which confirms this view, and that is its vapour-density. Experiments, and analyses made, lead the author to the formula $CH_3I + \frac{1}{2}CH_4O$. To decompose this body it is sufficient to treat it with water, which dissolves the methylic alcohol; the iodide of methyl left after washing and drying over chloride of lime boils at 43·1° under 761 m.m. There is therefore a difference of 5° between its boiling-point and that of the molecular compound.

Action of different Alcohols on some Acetals of the Monovalent Alcohols.— Marcel Delépine.—Already noticed.

Glucamine: a New Base derived from Glucose.— L. Maquenne and E. Roux.—Already noticed.

Synthesis and Properties of the Nitrile-phenols.— Edmond Fiquet.—Take equimolecular weights of cyanacetic acid and one of the benzylic, *o-m-p*-toluic, cinnamic, &c., aldehydes. This mixture is placed in a flask with a long neck and the temperature raised to about the boiling-point of the aldehyde, then wait till the reaction commences; this takes place with the evolution of heat and steam. Withdraw the gas-burner, and allow the reaction to terminate spontaneously. The crystalline mass which forms on cooling is then purified by crystallisation in alcohol. To transform these bodies into nitriles with the normal chain, they are heated *in vacuo*. The body commences by melting, carbonic acid is then given off; when this ceases, the temperature is raised and the nitrile distilled. These phenols, when introduced into the organism, not only prevent the development of micro-organisms, but also neutralise the action of their products of secretion.

The Tetrachlorised Dimethyl and Diethylamidobenzoylbenzoic Acids and their Derivatives.—A. Haller and H. Umbgrove.—The examination of these acids shows that they occur under identical conditions under which the non-chlorised dialcoylamidobenzoylbenzoic acids are prepared; that they differ from these latter, inasmuch that they cannot be etherified directly by the ordinary method, and they do not give dialcoylaniline-phthaleins when we attempt to condense them with the dialcoylanilines by the help of acetic anhydride; that they form under these conditions tetrachlorised mixed acetyldialcoylamidobenzoylbenzoic anhydrides, and that these anhydrides, treated with alcoholates of sodium, give rise to other salts.

Action of Saccharine on the Urea from Phenylhydrazine.—H. Défournel.—Saccharine does not combine with ordinary urea, but it does so with the urea from phenylhydrazine. A cold saturated solution is made of one molecule of saccharine in pure methylic alcohol. To this solution, one molecule of urea from phenylhydrazine is added. A certain quantity of this urea remains undissolved; it must therefore be heated to effect the solution. On cooling, a pale rose-coloured crystalline compound is formed; this must be re-crystallised from boiling methylic alcohol. The crystals melt at 98°; they are soluble in boiling water, and on the aqueous solution cooling the substance is precipitated. The results of their analysis shows that an organic saccharinate has been formed:—

$$CO\begin{cases}NH-NH-C_6H_5\\NH-N=C_6H_5\end{cases}$$
$$C_6H_4\begin{cases}CO\\SO_2-NH_2\end{cases}$$

The Basic Saccharinate of Quinine.—H. Défournel.—When we mix a solution of two molecules of saccharine in ethylic alcohol with a warm solution of one molecule of quinine we obtain, on evaporation to dryness, a syrupy uncrystallisable body, slightly soluble in cold water, fairly so in hot water, and easily soluble in alcohol, ether, and chloroform. This body is the neutral saccharinate of quinine. The basic saccharinate of quinine is obtained by evaporating on the water-bath a mixture of an alcoholic solution of one molecule of anhydrous quinine with an alcoholic solution of one molecule of saccharine; as in the former case, a syrupy non-crystallisable mass is obtained. The basic saccharinate of quinine can, however, be obtained in the crystalline form by following the general method for the preparation of the metallic saccharinates, which consists in effecting the double decomposition of saccharinate of soda and the metallic sulphates in aqueous alcohol, only, the metallic sulphate is replaced by sulphate of quinine.

MISCELLANEOUS.

The Ceric Sulphates.—W. Muthmann and L. Stützel.—The authors have repeated the analysis of these sulphates, about which such different opinions exist. The evaporation of a solution of ceric hydrate in dilute sulphuric acid always gave them a yellow salt in the form of fine needles; this was followed, but not always, by another reddish-brown salt in large crystals, this latter being decomposed by pure water. The yellow salt is ceric sulphate, $(SO_4)_2Ce+4H_2O$; the yellowish-brown salt is a ceroso-ceric sulphate, $(SO_4)_3Ce_2{}_1{}_2(SO_4)_2Ce+20H_2O$.—*Berichte*, vol. xxxiii., p. 1763.

The Quantitative Estimation of Ozone.—O. Brunck. In this paper the author describes the difficulties to be met with in the analysis of ozonised gases. By means of a series of experiments on the action of ozone on a neutral solution of iodide of potassium he arrives at the following practical conclusions:—1. The quantitative estimation of the proportion of ozone in a gas by means of a neutral solution of iodide of potassium leads to incorrect results, which are much too low. 2. Exact results can be obtained by using an acid solution of iodide of potassium. It is only when using a very concentrated solution that a small error is to be feared in consequence of the formation of hydriodic acid. This, however, can be allowed for by making a simultaneous blank experiment. 3. It does not matter whether sulphuric or acetic acid be used, but it is advisable always to use the calculated quantity of acid.—*Berichte*, vol. xxxiii., p. 1832—1842.

Wanted, Assistant for Research work, chiefly Organic, for a few months.—Apply by letter to H. Auden, Woodford Green, Essex.

Young Chemist (Organic), Ph.D., with knowledge of Physical Chemistry and Bacteriology, seeks employment with Analyst or in Works.—Address, Y. C., Chemical News Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

FOR SALE.—"Chemical Society Journals." Complete set (unbound), with Indices, 1875—1901. Best offers. Address, E., Chemical News Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C,

FOR SALE.—A very fine 1-25th Best Achromatic Objective, by Ross, of London. Cost £24, price £10. Can be seen at the Office of Mr. L. F. St. John, 33. Havelock Road, Hastings.

BOROUGH OF SOUTHWARK.

APPOINTMENT OF PUBLIC ANALYST.

The Council are desirous of receiving applications for the Appointment of PUBLIC ANALYST for the Borough from persons not exceeding 45 years of age.

The appointment will be subject to the approval of the Local Government Board.

Candidates must furnish proof of competent skill and knowledge of Analytical Chemistry, Therapeutics, and Microscopy, and must be holders of the diploma of Fellowship or Associateship of the Institute of Chemistry of Great Britain and Ireland, together with the Certificate granted by the Institute after an examination conducted by them in Therapeutics, Pharmacology, and Microscopy, and be competent to discharge the duties in accordance with the Sale of Food and Drugs Acts, 1875 to 1899.

The salary will commence at £400 per annum, rising by annual increments of £25 to a maximum of £500 per annum, the Council providing a laboratory, apparatus, and all necessary assistance at a cost not exceeding £300 per annum.

The person appointed will be required to devote the whole of his time to the service of the authority and discharge such duties as they may require. The appointment will be made on the understanding that there will be no pension or superannuation allowance.

Forms of application with particulars of the appointment may be obtained from the undersigned.

Applications on the prescribed form, accompanied by not more than three testimonials, and endorsed "Public Analyst," must be sent to me not later than 4 o'clock on Wednesday, the 20th day of November 1901.

Personal canvassing will disqualify.

J. A. JOHNSON,
Town Clerk.

Southwark Town Hall,
Walworth Road, S.E.,
November 6, 1901.

THE CHEMICAL NEWS.

Vol. LXXXIV., No. 2190

ON THE PLACE OF HYDROGEN IN THE PERIODIC SYSTEM.

By BOHUSLAV BRAUNER, Ph.D., F.C.S.

Within recent times Mr. Masson's view that hydrogen is the first member of the halogen group has been preferred by such eminent chemists as Sir William Crookes and Professor Ramsay to the old view that it stands at the head of the first group in the periodic system.

Professor Ostwald in his recently edited "Grundlinien der Anorganischen Chemie," the most modern of all books on inorganic chemistry, in which, however, the periodic system is *not* taken as a basis of the treatment of elements, but only brought in an appendix, also places hydrogen at the head of the halogen group. It may be mentioned that Ostwald places the elements Cu, Ag, Au in two quite different groups, and that he has introduced a new group for "other elements," many of which might have very well been placed in natural groups corresponding to those of the periodic system.

It has been for some time my intention to express my opinion on this important question, and I am very glad that this question was treated quite recently by Mr. Geoffrey Martin (Chem. News, lxxxiv, pp. 154—155).

While agreeing with most of Mr. Martin's arguments I do not partake his view that "it is needless to give any other examples"; for such an important and by no means simple question ought to be treated as fully as possible in order to prove definitely that only the older view is correct, whereas the view recently proposed is quite untenable.

Before bringing our own arguments let us see first what is the opinion of the chemist who may be regarded as the real founder of the periodic system of elements, and, as I may say, of the modern part of chemistry connected with it. Undoubtedly, chemical elements had been arranged long before Mendeleeff in a manner approaching more or less our present form of the periodic system, but all these arrangements possessed not much more than the outer form, whereas Mendeleeff established his periodic law:—"The properties of elements and of the simple and compound bodies formed of them, as well as the combining forms of elements, are periodic functions of the atomic weights," and by saying, "it will be impossible in the future to consider chemical elements and their compounds without taking the periodic system (and the periodic law) as a point of departure," he opened up anew the old department of inorganic chemistry, the interest for which had nearly vanished in comparison with the astonishing development of modern organic chemistry, worked up upon the basis of the doctrine of valency and chemical structure.

Everyone knows what a great help the periodic system has proved in teaching and studying chemistry, and especially those who are survivors of the ante-Mendeleeffian period, are aware of the incomparably greater pleasure and satisfaction which is afforded by the experimental work in inorganic chemistry, since we are able to conduct it in the spirit indicated by Mendeleeff. Modern physical chemistry with its new methods and views has, of course, greatly contributed to the *renaissance* of inorganic chemistry, but it is not the place to dwell upon this question here.

1. Mendeleeff does not simply place hydrogen "at the head of the alkali metal group," as Mr. Martin does; on the contrary, he shows that there is a marked difference between hydrogen and the latter, for he speaks in his well-known fundamental paper of the difference between the "typical elements" and the other elements of the same group; the former exhibiting, like the first members of the homologous series of organic compounds, some properties which are not found in the higher members, and *vice versâ*. "From this follows the *isolated, independent position of hydrogen* with the lowest atomic weight." "According to the (combining) form of its salt-like oxide, H_2O, and the salts HX it must stand in the first group; the nearest analogue of H is Na, which also stands in an *odd* series of the first group. The more remote analogues of H are Cu, Ag, Au."

I cannot repeat all he says about the later elements. It must suffice to say that they occupy a double position, in the *first* group and in the *eighth* group; in the lowest combining forms they correspond to H and Na (first group). In spite of a similarity of the combining forms, HX and NaX, there exists between both a whole series of generally known differences, the differences between carbonic acid and the homologous glycolic acids being similar to it in many respects.

As regards the similarity of the physical properties of the compounds of H′ and Na′, Cu′, Ag′, and Au′ he shows that their monochlorides have a molecular volume, very nearly equal, varying only between 26 and 29, whereas the volumes of LiCl and KCl, *not belonging to this sub-group*, are 21 and 37. The same holds good in the case of other compounds.

All this shows that hydrogen does not simply stand "at the head of the alkali metal group."

2. According to Mendeleeff there are two kinds of oxides which must be strictly distinguished from another, viz., (*a*) the oxides of the water type, and (*b*) the oxides of the hydrogen peroxide type.

Among both kinds are found oxides behaving as *peroxides*. They are distinguished from ordinary oxides by possessing one or more "active" oxygen atoms, and by liberating from hydriodic acid an amount of iodine equivalent to the "active" oxygen. The peroxides of the water type are called by Schönbein *ozonides* (*e.g.*, CrO_3, Pb_2O_4, Tl_2O_3, Ce_2O_4, Pr_2O_4, &c.), whereas those of the hydrogen peroxide type are called *antozonides* (*e.g.*, Na_2O_2, BaO_2, TiO_3, La_2O_5, Th_2O_7, UO_4, &c.).

Now the composition of all oxides of the water type, including the *ozonic* peroxides, is the *measure of valency* of the elements contained in them in combination with oxygen, which later is here normally divalent, whereas from the *antozonic* peroxides no conclusions as to the valency of the respective elements can be made, some of their oxygen atoms being apparently monovalent.

Mendeleeff has shown that the quantity of oxygen combined with two atoms of an element in oxides of the water type, including several "ozonides," reaches maximally the number of the group of the periodic system, in which the respective element stands; such oxides being called "limit compounds" (*e.g.*, Tl_2O_3—III., Pb_2O_4—IV., Cr_2O_6—VI., Cl_2O_7—VII., Os_2O_8.—VIII), whereas the antozonic peroxides may be regarded as a kind of "ultra-limit compounds."

It is a general rule that an element which forms an antozonic peroxide in no case forms another oxide or ozonide of the water type containing a higher number of oxygen atoms than the antozonic peroxide.

It must first be admitted that the circumstance that there is an *enormous, thorough difference in chemical character* between hydrogen and the halogens, between their ions and between H_2O and the oxides of the halogen group, like Cl_2O, between the compounds of hydrogen and those of the halogens with the metallic and non-metallic elements, constitutes a powerful argument against the position of hydrogen at the head of the halogen group. How can such a positive element as hydrogen stand at the head of such negative elements as the halogens?* The maximum

* The elements standing at the head of a sub-group are *always* more negative or less positive than the higher members of that sub-group.

valency of chlorine = 7 is reached in Cl_2O_7, whereas the highest *hydrogen* oxide of the water type is water itself, in which hydrogen is undoubtedly monovalent. In hydrogen peroxide hydrogen has no higher valency than *one*, and so the composition of water, *which is a limit compound of hydrogen*, indicates that hydrogen is *in maximo* monovalent. Hydrogen, therefore, cannot belong to the chlorine group, the limit compounds of which correspond to the valency = 7.

The objection that fluorine also has no higher valency than *one* is met by pointing to the circumstance that we do not know any oxygen compound of fluorine, and are therefore unable to speak of its valency towards oxygen. But fluorine, as a "typical element," possesses properties lying between those of the other halogens and those of the "typical" oxygen, which latter in closest analogy to the monovalency of fluorine, is hardly ever more than divalent, though it stands at the head of the *hexad* group. And yet it is not improbable from the constitution of compounds like KF.HF and some double fluorides that fluorine sometimes possesses a higher valency than one, whereas in the case of hydrogen we have a *certainty* that its *maximum* valency is one.

I would like to meet with still another objection. The *odd* numbers of the first group of the periodic system form a series of *higher* oxides than water:—H_2O_2, Na_2O_2, Cu_2O_2, Ag_2O_2, Au_2O_2.

Why should we not regard *all* these oxides as possessing the same constitution, and *all* the elements themselves as higher than monovalent?

The answer is this:—The peroxides of hydrogen and sodium are ultra-limit compounds of *monovalent* elements of the *first group*, whereas the ordinary, respectively, ozonic oxides of copper, silver, and gold are divalent compounds of the elements of the *eighth group*. The maximum valency of these elements is probably *three* in copper (Cu_2O_3?), *two* in silver, and *three* in gold.

The circumstance that the position of hydrogen in its old, original place in the periodic system must be defended by rather complicated arguments, like the above, does, however, by no means prove that the view defended is incorrect.

Bohemian University, Prague.
October 22, 1901.

THE FREEZING-POINT OF VEGETABLE SAPS AND JUICES.

By WALTER F. SUTHERST, Ph.D.

THE injurious effect of frost on garden produce is a fact well known to gardeners and farmers, and it is at this time of the year especially when the precautions to counteract it are resorted to.

A temperature more or less below freezing-point must occur before any injury can be done, and this temperature is known to vary considerably for different species of plants. The degree of cold to which some plants can be subjected without damage is often very much below the freezing-point of the sap, which may be explained by the fact that liquids can be cooled much below their freezing-points without solidifying provided they are kept perfectly still—a condition usually present on a calm frosty night, —and then it is also possible for the sap to freeze and thaw again without any damage to the structure whatever.

This property of resisting frost induced me to find the freezing-points of the sap or juice of some of the more common vegetables and fruits, and the results agree pretty well with one's experiences in this matter.

The method adopted for these determinations was as follows:—An average sample of the vegetable or fruit—about half-a-pound—was reduced to a fine pulp by means of a grater; the mass then strained through muslin and filtered through thick filter-paper. Five c.c. of the sap were brought into a narrow test-tube containing a thermometer, and cooled down by a freezing-mixture of Glauber salts and concentrated hydrochloric acid. The results obtained were:—

	Freezing-point. °C.
1. Vegetable marrow—(*a*) Leaf and stalk ..	−0·75
(*b*) Fruit	−0·75
2. Swede turnip—(*a*) Leaf and stalk	−1
(*b*) Bulb	−1
3. Celery—(*a*) Green stalk and leaf	−1·4
(*b*) White portion	−0·75
4. Carrot—(*a*) Leaf and stalk	−1·2
(*b*) Root	−1·0
5. Cabbage—(*a*) Outside leaf	−1·1
(*b*) Heart	−0·85
6. Apple	−1·4
7. Pear	−1·75

It will be seen from the above figures that—(1) Those vegetables easily attacked by frost, *e.g.*, vegetable marrow, have the higher freezing-points; (2) the sap in the parts exposed to the air has the same freezing-point, *e.g.*, fruit and stalk of the turnip and marrow; while (3) those plants which have a portion in the ground, *e.g.*, celery and carrot, or protected, *e.g.*, cabbage heart, the sap in these portions freezes sooner than the exposed. It is very possible that these differences can be accounted for by the fact that the hardy exposed parts contain a more concentrated sap, since more evaporation goes on there; also, pear-juice, containing more dissolved uncrystallised matter, freezes lower than apple-juice.

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RESEARCH ON THE OXIDES OF CHLORINE.

By A. REYCHLER.

To facilitate the checking of calculations I will first give a few data as to the strength of my titrated solutions. The solution of thiosulphate of sodium is decinormal; 1 c.c. is equivalent to 0·00355 grm. of chlorine (or 0·008 grm. of bromine, or 0·012685 grm. of iodine), and corresponds to 0·00135 grm. of peroxide of chlorine. The solution of permanganate of potash is also decinormal; 1 c.c. is equal to 0·0008 grm. of oxygen, and corresponds to 0·0039 grm. of peroxide of sodium, or again to 0·0023 grm. of sodium (peroxidised).

I. *Peroxide of Chlorine and Caustic Potash.*

Preparation of a Solution of ClO_2.—220 c.c. of water were poured into a well-covered crystallising dish, and on the surface of the water a crucible was floated, containing 12 grms. of potassic chlorate treated with a cooled mixture of 44 c.c. of sulphuric acid, and 10 or 11 c.c. of water. The cover was then put on, and the action allowed to proceed for two hours. The water takes a yellow colour owing to the absorption of the gas produced, and the solution becomes of such a strength that 10 c.c. is equal to from 40 to 55 c.c. of thiosulphate; that is to say, from 0·0540 to 0·0742 grm. of ClO_2.* Under the above mentioned conditions, and at a temperature of 20°, accidents are of very rare occurrence. It did happen, however, that on one occasion when I had taken particular care to pulverise the chlorate very finely, the ClO_2 came off very rapidly, and terminated in an explosion.

The reaction between the peroxide of chlorine and the caustic potash is far from being instantaneous. When we

* A little hydrochloric acid is added to a solution of iodide of potassium, and then 10 c.c. of the solution of peroxide of chlorine. It is then titrated with the thiosulphate.

mix equimolecular solutions of the two substances (we can even use a slight excess of potash) the yellow colouration of the chlorinised gas persists for a considerable time. The chlorometric value of the mixture, shown in c.c. of thiosulphate, diminishes at first fairly rapidly, but the retrogradation becomes slower and slower, and the real value is not actually obtained until after several hours.

The following are the figures obtained from an experiment:—

To 20 c.c. of a solution of peroxide of chlorine, which equalled 880 c.c. of thiosulphate, and, consequently, contained 1·1880 grms. of ClO_2, I added 18·6 c.c. of a normal solution of caustic potash (that is, 1 c.c. more than the theoretical quantity).

The chlorometric value of the mixture varied in the following manner:—

Time elapsed.	10 c.c. were equal to—Thiosulphate. C.c.	The 218·6 c.c. were equal to—Thiosulphate. C.c.	Colour of the mixture.
1·5 mins.	21·7	474	Intense yellow.
9·5 ,,	17·9	391	—
17 ,,	17·3	378	—
30 ,,	16·7	365	—
1 hr.	16·2	354	—
5 ,,	15·8	345	Pale yellow.
23 ,,	15·7	343	Practically colourless.

Thus, as we should expect, according to the well-known equation, $2ClO_2 + 2KOH = KClO_2 + KClO_3 + H_2O$, the chlorometric value of the whole goes down to about four-tenths of the initial value of ClO_2 used in the experiment: $-880 \times 0{\cdot}4 = 352$.*

The concordance between what was foreseen theoretically and what actually occurred, seems quite sufficient when we consider that peroxide of chlorine generally contains a trace of free chlorine, and that during the operation described it is also partially decomposed into its constituent elements. The principal reaction is thus more or less complicated by the secondary transformations, $Cl_2 + 2KOH = KCl + KOCl + H_2O$ and $2ClO_2 = Cl_2 + 2O_2$, of which the first tends to keep the original chlorometric value constant, while the second produces an excessive retrogradation.

Remarks. — 1. When the amount of potash is exaggerated (by taking, for example, eight times the theoretical quantity), the yellow tint lasts for a much shorter time, and the final value is established much sooner. The resulting solution has the property of decolorising a solution of indigo-carmine (an indication of the presence of a hypochlorite), but it does not turn iodised paper blue, on account of the too great predominance of KOH. By the addition of hydrochloric or sulphuric acid it turns yellow very markedly, but acetic acid only causes a very slight change of colour.

2. If, instead of caustic potash, we substitute bicarbonate of potassium the reaction is retarded enormously.

II. *Peroxide of Chlorine and Peroxide of Sodium.*

While the transformation we have just described takes place with characteristic slowness, that which we are now coming to is instantaneous.

When a yellow solution of ClO_2 is added to a colourless solution of Na_2O_2 the mixture remains yellow so long as the second reagent is present in insufficient quantity; and it is not difficult to find experimentally, to within a drop or two, the quantity of Na_2O_2, which is exactly necessary to produce the decolouration. The operation can also be performed in the inverse sense, and the exact amount of ClO_2 determined, to cause the commencement of the yellow tint with a known quantity of sodic peroxide. These two operations can be carried out with the same precision as a titration.

The reaction is accompanied with the evolution of oxygen, and the resulting solution possesses the following properties:—It is faintly alkaline (that is, if it has not previously been made acid), it has no action either on indigo-carmine or on iodised starch paper. It becomes distinctly yellow on the addition of hydrochloric or sulphuric acid, and to a much less marked degree with acetic acid. When acidulated with a trace of the latter acid, it decolorises indigo, turns iodised paper blue, and with nitrate of lead gives the characteristic precipitate of plumbic chlorite, viz., crystalline flakes of a sulphur-yellow colour, very light, and with a very brilliant lustre.

To carry out the quantitative study of the reaction I made use of a special piece of apparatus, consisting of a graduated burette, connected by a flexible tube at the bottom to a movable reservoir; at the top of the burette there is a glass tap, connected by another flexible tube, to a bottle fitted with a cork pierced with two holes; a funnel with a tap passes through the other hole. Before commencing the experiment the burette is filled with water right up to the tap at the top, which must be then closed; the bottle contains a measured quantity of a solution of peroxide of sodium. The apparatus is then connected together, and a known volume of a solution of peroxide of chlorine is run into the funnel with the tap closed. The operation then consists of opening the tap at the top of the burette, and regulating the flow of ClO_2 from the funnel so that it is just sufficient to produce a yellow tint in the bottle. At the same time the gas generated is helped to escape by shaking the bottle, and equalising the water levels in the burette and the movable reservoir by gradually lowering the latter. When the volume of gas appears to be constant the upper tap can be closed, the bottle uncorked, and the contents analysed. Firstly, the chlorometric value of the solution is obtained, after being decolorised, if we like, with a drop of the solution of peroxide of sodium. Then the quantity of oxygen given off is measured by the difference found between the volume of the water displaced in the gasometric burette and the volume of the portion of the ClO_2 solution used. To effect this the volume of the unused portion of this solution is measured; that is the part left in the funnel.

The following figures were obtained by this method:—

Solution of Peroxide of Sodium.—Ten c.c. were equal to 47·95 c.c. of permanganate, and, consequently, contained 0·1870 grm. of Na_2O_2. Amount of this solution used, 10·1 c.c., contained 0·18887 grm. of peroxide (0·0775 grm. of oxygen).

For a special reason, which I shall explain later on, I did not here pay any attention to the caustic soda due to the solution of peroxide.

Solution of Peroxide of Chlorine.—Ten c.c. were equal to 43·8 c.c. of thiosulphate, and contained 0·05913 grm. of ClO_2.

The quantity of this solution used up was 55·55 c.c., equal to 243·3 c.c. of thiosulphate, or 0·32845 of ClO_2.

In the operation described I caused 67·5 parts of ClO_2 to react on 38·8 parts of Na_2O_2. The equation $2ClO_2 + Na_2O_2 = 2NaClO_2 + O_2$ gives practically the same proportion, viz., 67·5 to 39.*

Oxygen given off.—58·75 c.c. at a temperature of 16°, under 670 m.m., that is 0·0779 grm. This weight is equal to that of the oxygen in the peroxide of sodium.

Chlorometric Value of the resulting Solution.—Ten c.c. of this solution were equal to 28·7 c.c. of thiosulphate according to the two methods:—1. Ordinary direct titration. 2. Addition of an excess of hydrochloric acid and distillation of the chlorine to be estimated. 65·65 c.c. of the solution corresponded, therefore, to 188·4 c.c. of thiosulphate; and as the ClO_2 used was equal to 243·3 c.c. of the titrated liquor, the chlorometric value of the whole decreased to about eight-tenths of its original value. Everything thus happened according to the equation pro-

* 2 ClO_2 is chlorometrically equal to 10 Cl, while $KClO_3$ is only equal to 4Cl. I have made quite certain by direct experiment that the presence of $KClO_3$ only affects the titration very slightly.

* The figures given can be relied upon, as also can the calculation, which is too long to be reproduced here, that the ClO_2 used only contained a minimum quantity of free chlorine.

posed above, and the final solution contained an alkaline chlorite.

Remarks.—When we dissolved peroxide of sodium we always observe, even when using very cold water, a fairly considerable evolution of oxygen, and the solution continues to decompose slowly, as is shown by the persistent formation of bubbles of gas. This solution, therefore, contains not only the actual peroxide but also some caustic soda. I have always been of the opinion that the presence of this latter body has no great influence on the reaction of which we have just established the formula, and I base my opinion on the relative slowness of the reaction which might take place between the peroxide of chlorine and the alkaline base.

III. *Halogen Elements and Peroxide of Sodium.*

The action of chlorine, bromine, and iodine on an alkaline solution of peroxide of hydrogen has already been the subject of much research, as can be seen by referring to the "Handbuch der Anorganischen Chemie," by Dammer (vol. i., p. 435), and also Baumann's papers in the *Berichte*, 1891, iii , p. 789. This action is so similar to that of peroxide of chlorine that I was induced to confirm it by several experiments. The following are the results I obtained with *iodine* by making this element react on a calculated quantity of the other reagent.

Solution of Peroxide of Sodium. Alkalimetry.—100 c.c. were neutralised by 21·26 c.c. of normal acid, and consequently contained 0·4890 grm. of *sodium*.

Titration with Permanganate.—100 c.c. of the solution under experiment corresponded to 166 c.c. of permanganate, and contained 0·3818 grm. of peroxidised *sodium*. The rest of the metal—that is, 0·1072 grm.—was in the state of hydroxide.

Solution of Iodine (and Iodide of Potassium).—100 c.c. were equal to 209 c.c. of thiosulphate, and contained 2·6512 grms. of free iodine.

As we did not succeed in determining *experimentally* (as in II.) the proportion in which it was best to mix the reacting substances, I had recourse to the following calculation:—For 23 parts of sodium, 126·85 parts of iodine were necessary; 100 c.c. of the sodic solution (0·4890 grm. of the metal) thus corresponded to 101·7 c.c. of the iodine solution (2·6969 grms. of the halogen element).

The mixture causes an abundant disengagement of oxygen, and the resulting solution was of a reddish colour and had a faintly alkaline reaction. It did not require to be acidulated to decolorise indigo-carmine or turn iodised paper blue; it contained a certain quantity of hypoiodite. This latter salt evidently resulted from the action of the iodine on the soda; and, as 100 c.c. of our solution of alkaline peroxide contained 0·1072 grm. of hydroxidised *sodium*, a quantity of iodine weighing 0·5912 grm. and equal to 46·6 c.c. of thiosulphate could be detected by titration. In fairly good concordance with this theory, I found that 201·7 c.c. of the final solution was equal to 49 c.c. of thiosulphate.

As to the evolution of oxygen, I measured it in a special experiment, similar to that described in Part II. With 100 c.c. of solution of sodic peroxide and 101·7 c.c. of iodine solution, I obtained, at 15° under 760 m.m., 202 c.c. of oxygen; that is, 0·269 grm. of the gas. The weight of oxygen contained in the peroxide used for the experiment was 0·266 grm.

The result of these operations shows that the action of iodine on a partially decomposed solution of peroxide of sodium should be formulated in the following manner:—

Principal reaction .. $Na_2O_2+I_2=2NaI+O_2$
Secondary reaction .. $2NaOH+I_2=NaI+NaOI+H_2O$

The colour of the solution seems, further, to indicate that a small quantity of iodine remains free, and that a corresponding quantity, therefore, of peroxide ought to react on the hypoiodite, giving iodide, oxygen, and the free base.

Chlorine and bromine have been the subject of similar experiments, but I need not go into details. Suffice it to say that the results obtained with alkaline solutions confirm the general character of the equation $Na_2O_2+E_2=2NaE+O_2$, in which E represents chlorine, bromine, or iodine. By comparing this conclusion with that arrived at in Part II., we see that E not only represents a halogen element, but also the group ClO_2 of peroxide of chlorine.—*Bull. Soc. Chim.*, Series 3, vol. xxv., No. 13.

THE QUANTITATIVE SEPARATION AND DETERMINATION OF URANIUM.*

By EDWARD F. KERN.

(Continued from p. 226).

Part I.—Separation of Uranium (*continued*).

Separation of Uranium from the Alkali and the Alkaline Earth Metals.

If a solution containing uranium, alkalis, and alkaline earths is precipitated with ammonia, a portion of the alkalis and alkaline earths is carried down by the ammonium uranate (Fresenius's "Quantitative Chemical Analysis," Sixth Edition, p. 533), thus preventing a complete separation.

Hillebrand (*Amer. Journ. Sci.*, 1900, x., 136) found that it is possible to completely separate uranium from the alkalis and alkaline earths by several precipitations with ammonia. In order to verify this statement, solutions containing a measured amount of standard uranium nitrate solution, and sodium and potassium salts, were precipitated by means of a slight excess of ammonia, and the solutions brought to boiling. The precipitates were washed with a warm 2 per cent solution of ammonium chloride, after which they were dissolved from the filters with warm hydrochloric acid (sp. gr. 1·10), and caught in beakers. The precipitation of the uranium by ammonia, in the presence of ammonium chloride, and from hot solutions, was repeated twice, and it was found that after three precipitations the ammonium uranate was free from alkalis.

Magnesium may be separated from uranium by means of ammonium sulphide in the presence of ammonium chloride (*Zeit. Anal. Chem.*, 1865, iv., 384), and also by ammonia in the presence of an excess of ammonium chloride. The latter method is the one ordinarily used (Fremy's "Encyclopédie Chimique," 1884, p. 86). To the solution containing uranium and magnesium, add ammonium chloride, and boil. When the solution becomes clear, add a slight excess of ammonia to the hot solution, and continue boiling for a few minutes. Filter while hot, and wash the precipitate with hot water containing ammonium chloride. Dry, ignite, and weigh the uranium as oxide.

The separation of uranium from barium, strontium, and calcium is usually done by means of sulphuric acid in the presence of alcohol (Fremy's "Encyclopédie Chimique," 1884, p. 86). The metals should be in solution as chlorides, having present the smallest possible amount of free hydrochloric acid. To the moderately dilute solution, add sulphuric acid, then alcohol, which precipitates the barium, strontium, and calcium, in the form of sulphates. The uranium in the filtrate is precipitated with ammonia, and weighed as oxide.

The separation of uranium from barium, strontium, and calcium, may be brought about by precipitating the uranium with freshly prepared ammonium sulphide (free from carbon dioxide) (Fresenius's "Quantitative Chemical Analysis," p. 534).

In 1885, G. Alibigoff studied the action of mercuric oxide on uranium solutions, and found a means of

* Contribution from the Havemeyer Laboratories of Columbia University. From the *Journal of the American Chemical Society*, xxiii., No. 10.

separating uranium from the alkalis and alkaline earths (*Liebig's Ann. Chem.*, 1886, ccxxxiii., 147). He showed that neither ammonium sulphide, nor ammonium carbonate followed by ammonium oxalate, can be successfully employed for separating uranium from calcium. The latter method is, however, preferable to the first. He states that a complete separation of uranium from calcium, strontium, magnesium, and the alkalis can be effected by the use of mercuric oxide; it does not, however, afford a separation of uranium from barium. The precipitation is made by adding a slight excess of freshly prepared mercuric oxide (in the form of an emulsion) to the boiling solution which contains ammonium chloride or nitrate. The boiling is continued for a few minutes longer, and then rapidly cooled by placing the vessel into cold water. Wash the precipitate by decantation with a cold dilute solution of ammonium chloride. It is placed along with the filter in a platinum crucible, cautiously heated at first, after which the temperature is gradually raised, and finally ignited over a blast-lamp. The residue consists of pure U_3O_8. The separation of uranium from the alkali metals by this method does not give any undue trouble, but when calcium and strontium are present they are rather hard to rid from the uranium precipitate. This difficulty is overcome by boiling several times, during washing by decantation, with a solution of ammonium chloride, and each time rapidly cooling the solution before pouring off the supernatant liquid. The calcium and strontium in the filtrate are determined by the ordinary methods after the removal of the mercury by hydrogen sulphide.

Separation of Uranium from the Alkali and Alkaline Earth Metals by Electrolysis of Acetate Solution.

Uranium is a very difficult metal to separate from the alkalis and alkaline earths by gravimetric methods; but by electrolysing an acetate solution of these elements a perfect separation can be effected (*Amer. Chem. Journ.*, 1879, i., 329; *Journ. Amer. Chem. Soc.*, 1898, xx., 279). It can be readily separated from sodium, potassium, rubidium, cæsium, magnesium, calcium, strontium, and barium. This method was used by E. F. Smith for separating uranium from the alkalis, the alkaline earths, and the rare earths in the analysis of certain rare minerals.

A very peculiar property of uranium is that it is not deposited as metal on the cathode, but as the hydrated protosesquioxide. Molybdenum is the only other metal known which, like uranium, is deposited as oxide on the cathode.

Experimental.

This research was made in order to fully confirm the reliability of the electrolytic method for the estimation of uranium and its separation from the alkalis, and also to find the conditions which are best suited for rather dilute solutions.

The cathodes for the first six experiments, when a current of $N.D_{140}=0.6$ to 0.7 ampère was employed, were two platinum dishes of about 250 c.c. capacity. For experiments Nos. 7 to 10, the cathode was a platinum dish of about 150 c.c. capacity.

The anodes were made of heavy platinum wire. One was made of 30 c.m. of No. 12 gauge platinum wire wound into a flat spiral of 4 c.m. diameter. The other anode was made of 37 c.m. of No. 14 gauge platinum wire wound into a flat spiral of 4 c.m. diameter. The results obtained by the use of either anode were the same,

Storage cells were the source of current.

For the electrolysis, a measured amount of standard uranium nitrate solution was run into a cleaned and weighed platinum dish. A known amount of sodium acetate and of acetic acid was added, and the solution diluted to a definite volume. After heating to about 60° C., the current was started, and the electrolysation continued till the solution was clear and colourless, and no uranium was indicated when about 2 c.c. of the electrolyte was removed and tested with potassium ferrocyanide in the presence of hydrochloric acid. As soon as all the uranium was precipitated, the current was interrupted and the electrolyte was emptied into a beaker. The black deposit was several times washed with warm distilled water. The electrolyte and washings were then poured through a fluted filter, so as to prevent the loss of any particles of the deposit which are apt to be removed during washing. The filter was washed with warm water, dried over a Bunsen flame, ignited, and added to the dish. The dish was ignited at "redness" for about fifteen minutes, after which it was allowed to cool in a desiccator. The dish was weighed, and the final weight taken when it had remained on the balance pan for about five minutes, thus allowing its weight to become constant.

The deposit consisted principally of black hydrated protosesquioxide of uranium ($U_3O_4.3H_2O$), which on ignition changed to U_3O_8.

At the beginning of the electrolysis the deposit formed as yellow uranic hydroxide, but as the deposition continued it changed to the black hydrated protosesquioxide.

The results obtained* are given in Table II.

These results were obtained by electrolysing a solution of 200 c.c. volume with a current of $N.D_{140}=0.55$ to 0.65 ampère.

The results obtained, when a solution of 125 c.c. was electrolysed with a current of $N.D_{100}=0.70$ to 1.50 ampère, are given in Table III.

According to the above results, the best conditions for the electrolytic precipitation of uranium from a rather dilute acetate solution are as follows:—To the solution containing about 0.10 grm. of U_3O_8 add from 1 to 2 grms. of sodium acetate (if alkalis are present, no sodium acetate is needed), and from 1 to 2 c.c. of 50 per cent acetic acid, or if glacial acetic acid is used only half the quantity is needed. Dilute to from 125 to 200 c.c., heat to about 65° C., and electrolyse with a current of $N.D_{140}=0.60$ to 0.70 ampère, and 6 to 8 volts. The uranium is completely precipitated in from five to seven hours.

With solutions containing about 0.15 grm. of U_3O_8 more current is necessary, and the best conditions are:—Add from 1 to 2 grms. of sodium acetate, and from 1 to 2 c.c. of 50 per cent acetic acid, dilute the solution to 125 c.c., and electrolyse with a current of $N.D_{100}=$ from 0.70 to 1.0 ampère. The temperature of the solution should be about 65° to 70° C. After the current is started no heat need be applied outwardly, as the current itself keeps the solution heated. The time required for the complete precipitation of about 0.15 grm. of U_3O_8 is from six and one-half to seven and one-half hours.

When solutions containing more than 0.15 grm. of U_3O_8 were electrolysed, some difficulty was experienced in precipitating all within eight hours by a current not exceeding $N.D_{100}=1$ ampère. With a current greater than this the deposits were very spongy, and peeled from the dish; so the amount of U_3O_8 in solution should not exceed 0.15 grm.

The electrolytic precipitation of uranium has been used a number of times for the estimation of uranium and for separating it from the alkalis and alkaline earths. The results obtained were concordant with those obtained by precipitating it gravimetrically.

The simplicity of the electrolytic method for the determination of uranium, and the short time required, are in favour of this method.

Separation of Uranium from Phosphoric Acid. Review of Methods.

Reynoso's Method (*Liebig's Ann. Chem.*, 1852, lxxxi., 368).—The uranium compound should be in solution as nitrate, having a small amount of free nitric acid present. Dilute to about 150 c.c., add a strip of pure metallic tin, and boil. The phosphoric acid unites directly with the tin, to form oxyphosphate of tin, which is insoluble. The

* This part of the work, including experiments 1—6, was done under the direction of Prof. E. F. Smith at the University of Pennsylvania, during April, 1900.

TABLE II.

Experiment No.	Grms. of sodium acetate.	Amount of glacial acetic acid.	Dilution.	Current. Current N.D.$_{140}$ = ampère.	Volts.	Temperature.	Time, in hours.	Theoretical amount of U_3O_8 taken.	Weight of deposited U_3O_8.
		C.c.	C.c.			°C			
1.	2	0·7	200	0·55	5	68—70	8	0·1098	0·1095
		Drops.							
2.	2	12	200	0·60	5	70	7	0·1098	0·1097
		C.c.							
3.	2	0·5	200	0·60 - 0·65	8—6	68—75	5	0·1098	0·1100
4.	2	0·5	200	0·65	8—7·3	65—67	5½	0·1318	0·1319
5.	2	0·5	200	0·65	7·5—6	68—70	5	0·1318	0·1318
6.	2	0·5	200	0·60—0·65	8—5·5	69—71	5½	0·1318	0·1320

TABLE III.

Experiment No.	Grms. of sodium acetate.	Amount of 50 per cent acetic acid.	Dilution.	Current N.D.$_{100}$ = ampère.	Temperature.	Time, in hours.	Theoretical amount of U_3O_8 taken.	Weight of deposited U_3O_8.
		C.c.	C.c.		°C.			
7.	1·0	2	125	0·70—0·85	80—85	6	0·1361	0·1363
8.	2·0	2	125	0·70 - 0·93	70—80	6½	0·1814	0·1816
9.	2·0	2	125	0·95—1·50	70—75	7½	0·2268	0·2270
10.	0·3	1	125	0·90—1·30	73—80	8	0·2268	0·2260

precipitate is filtered off and thoroughly washed. The filtrate is made alkaline with ammonia, and the precipitate which forms is treated with acetic acid. If it does not entirely dissolve, nitric acid is added and the precipitation by pure metallic tin repeated (Fremy's "Encyclopédie Chimique," 1884, p. 86). Heat the solution to boiling, filter off the oxyphosphate of tin, and wash with warm water. The precipitate rarely contains any uranium. The tin in the filtrate is removed by means of hydrogen sulphide. The filtrate from the tin sulphide is boiled till all hydrogen sulphide is expelled, after which the uranium is determined by any of the ordinary methods.

W. Hintz (*Liebig's Ann. Chem.*, 1869, cli., 216) had occasion to investigate this method, and stated that a complete separation of phosphoric acid from uranium is effected by means of metallic tin.

Knopp and Arendt Method (*Chem. Centrbl.*, 1856, 773).—The separation of uranium from phosphoric acid may be effected by fusing the ignited mass of uranium and phosphoric acid with a mixture of potassium cyanide and potassium carbonate, and treating the fused mass with warm water to dissolve out the phosphoric acid as soluble alkaline phosphate. The uranium is left as protoxide, which is re-ignited and weighed, or else dissolved in acid and precipitated by ammonia. The phosphoric acid in the filtrate is precipitated with magnesia mixture and weighed as magnesium pyrophosphate. Hintz (*Liebig's Ann. Chem.* 1869, cli., 216) used sodium carbonate in place of potassium carbonate, and obtained very satisfactory results.

E. Reichardt's Method (*Zeit. Anal. Chem.*, 1869, viii., 116; *Bull. Soc. Chem.*, 1873, xx., 347) is based on the direct precipitation of phosphoric acid from an acetate solution as uranyl-ammonium phosphate, provided the uranium is in excess. The precipitate is filtered off, washed, dissolved in a solution of sodium carbonate, and the solution added to a solution of magnesia mixture, which precipitates the phosphoric acid as magnesium ammonium phosphate. If iron is present it is first precipitated from a nitric acid solution by adding an excess of sodium carbonate and boiling (*Zeit. Anal. Chem.*, 1869, viii., 116). The phosphoric acid in the filtrate is precipitated as magnesium ammonium phosphate, and the uranium determined by the ordinary method, after expelling all the carbon dioxide.

Fresenius and Hintz Method (*Zeit. für Analytische Chemie*, vol. xxxiv., p. 437; CHEMICAL NEWS, 1895, vol. lxxii., p. 206).—This method provides a means of separating arsenic and phosphoric acid from copper, uranium, and iron. Have the solution feebly acid with hydrochloric acid, add an excess of potassium ferrocyanide, then saturate with sodium chloride. The ferrocyanide of copper, uranium, and iron are washed by decantations and subsequently decomposed by a warm solution of caustic potash, changing them to hydroxides. Filter and wash with a dilute solution of ammonium chloride till no ferrocyanide is recognised in the washings. The mixed hydroxides are treated with dilute hydrochloric acid. If any residue remains it is decomposed by a warm solution of caustic potash, going through with the same treatment as before. The solution by hydrochloric acid is free from arsenic and phosphoric acid. The copper, iron, and uranium are separated by ordinary methods.

Friedel and Cumenge (*Am. J. Sci.*, 1900, x., 135) separated phosphoric acid from uranium by dissolving the substance in nitric acid, and precipitating the phosphoric acid with ammonium molybdate.

This method was used (at the University of Pennsylvania in 1900) for estimating the amount of phosphoric acid in precipitates of uranous phosphate, which were formed by electrolysis. The sample was dissolved in 30 c.c. nitric acid (sp. gr. 1·42) and 3 c.c hydrochloric acid (sp. gr. 1·20). When iron was present, the sample was dissolved in a mixture of 20 c.c. hydrochloric acid (sp. gr. 1·20) and 10 c.c. citric acid (sp. gr. 1·42). The solution was diluted to about 100 c.c., and nearly neutralised with ammonia. A few drops of nitric acid were added to clear the solution, making it slightly acid, then to the hot solution (not above 65° C.) 50 c.c. of molybdate solution* for every decigrm. of phosphorus pentoxide present. After digesting at 65° C. for an hour and a half, the yellow precipitate was filtered, and washed with cold water. The filtrate was tested for phosphoric acid by adding more molybdate solution and re-heating at 65° C. The yellow precipitate of ammonium phosphomolybdate was dissolved from the filter with ammonia and hot water, and washed into a beaker to a bulk not exceeding 100 c.c. It was nearly neutralised with hydrochloric acid, cooled, and magnesia mixture added, drop by drop from a burette, stirring all the while. After about twenty minutes, 30 c.c. ammonia (sp. gr. 0·96) were added and the solution allowed to stand in the cold for three hours. The precipitate of magnesium ammonium phosphate was filtered and washed with dilute ammonia (2·5 c.c. ammonia and 100 c.c. water) till free from chlorides. The precipitate was dried, ignited, and weighed as magnesium pyrophosphate

* Prepared according to the formulæ given in the "Official Methods of the U.S. Agricultural Chemists."

The uranium in the filtrate, from the ammonium phosphomolybdate, was determined by three precipitations with ammonia, and weighed as U_3O_8.

(To be continued).

AMMONIUM PERSULPHATE AS A SUBSTITUTE FOR LEAD PEROXIDE IN THE COLORIMETRIC ESTIMATION OF MANGANESE.*

By HARRY E. WALTERS.

Almost everybody who has used lead peroxide in the colorimetric estimation of manganese has wished for a substitute which would dissolve completely in the acid solution, thereby allowing the comparisons to be made as soon as the solutions are cool. In the former method, it is necessary to use a centrifugal machine or allow considerable time for the finely-divided lead to settle. The substitute should be as cheap (or nearly so), act as rapidly, and be fully as accurate.

The writer has made a few experiments in the past with different substances, but without success, until, acting on a suggestion of Mr. Hugh Marshall's, which appeared in the Chemical News, vol. lxxxiii., p. 76, that ammonium persulphate could probably be used for the quantitative estimation of manganese colorimetrically. Some of the salt was obtained and experiments instigated to find the proper procedure.

In all attempts to use the salt in solution in conjunction with the nitrate of silver (which is essential), the results were not satisfactory, owing to the slow decomposition of the persulphate, or the precipitation of the silver as peroxide, but where the salt was used direct with the requisite amount of nitrate of silver, very satisfactory results were obtained.

As the presence of a silver salt is essential for the oxidation of the manganese to permanganic acid, experiments were made to find the amount which should be present, and finally it was found that where 0·02 grm. of nitrate of silver was present the oxidation was complete. If much less than this be used, the oxidation will not take place, and, if too much be present, silver peroxide will separate and give an off-coloured solution difficult or impossible to compare.

Finally, the following scheme was adopted:—0·2 grm. of the test steel, and a standard steel of known manganese contents, are weighed off into suitable test-tubes; 10 c.c. of nitric acid of 1·20 sp. gr. are added to each. The tubes are placed in a water-bath and heated until dissolved, and all nitrous fumes are driven off. Fifteen c.c. of a solution of nitrate of silver, equal to 0·02 grm. $AgNO_3$ (1·33 grms. of the salt to 1 litre of water), are added to the tubes in the bath. This will cool the solution considerably. Now add immediately about 1 grm. ammonium persulphate salt to each, and continue warming until the oxidation commences, and then for about a half minute longer. Remove the tubes from the baths while the evolution of oxygen continues, and place in a cold water-bath. When solutions are cool, which will require but a few minutes, they are compared as usual. In case the manganese is high in the sample, 0·75 per cent and upwards, 0·1 grm. of the sample is taken.

The procedure for pig-irons and blast-furnace cinders is the same as for steel until the sample is dissolved, except that the cinders should be moistened before the addition of the acid; when in solution they should be filtered, in order to free them from the suspended matter. The paper is then washed, using the 15 c.c. of nitrate of silver solution as the wash, and the procedure continued the same as for steels. If this filtration is not made, the suspended matter (the carbon or silica), which in the old method is mechanically separated by the lead peroxide, would give an off-colour to the solution.

In dissolving shot or chilled iron samples, it has been found good practice to add a little persulphate to the acid solution. This will destroy the combined carbon and aid the solution of the sample.

The following comparative results by the lead peroxide and ammonium persulphate methods show how well the results agree:—

	Lead peroxide. Per cent.	Ammonium persulphate. Per cent.
Steels.		
1.	0·33	0·33
2.	0·38	0·39
3.	0·40	0·39
4.	0·47	0·46
5.	0·58	0·58
6.	0·67	0·67
7.	0·75	0·75
8.	0·80	0·80
Pig-irons.		
1.	0·32	0·30
2.	0·65	0·65
3.	0·65	0·65
4.	0·70	0·69
5.	0·71	0·70
6.	0·77	0·75
7.	0·98	0·98
8.	1·02	1·02
Cinders.		
1.	0·23	0·24
2.	0·30	0·32
3.	0·32	0·32
4.	0·35	0·36
5.	0·40	0·40
6.	0·49	0·50
7.	0·70	0·72
8.	0·72	0·75

In making up the nitrate of silver solution it is preferable to make a stock solution by dissolving 33·25 grms. of the salt in a half litre of water. Ten c.c. of this diluted to a half litre will give the solution as used.

During the course of the experiments one interesting peculiarity of the salt was observed. While this peculiarity may be confined to this particular lot of the salt in question, it may be worth while to mention it to save others from the aggravation it caused us, and that is that when the salt is damp the reaction is very sharp and quick, but, when dry, it is very incomplete and irregular and not to be depended upon.

Ten one-pound bottles of the salt was the original order, and as soon as it was received the experiments were immediately commenced, correct results being obtained from this bottle and the following one. The balance had been stored in a rather warm place, and on opening the third bottle for use, trouble immediately commenced. After exhausting all seemingly possible and impossible causes, it was finally remembered that the salt in the previous bottles was damp, and 10 c.c. of water were added to the bottle, and intimately mixed with the salt. The trouble immediately disappeared. On drying some of the same salt it reappeared, so that now, a day or so before use, 10 c.c. of water are added to each one-pound bottle of the dry salt.

The advantages claimed for the ammonium persulphate method are:—

1st.—All the solution is obtained, there being nothing from which to decant, and the tube can be rinsed into the comparing tube.

* A Paper read before the Chemical Section of the Engineers' Society of Western Pennsylvania, September 19th, 1901. From the *Proceedings of the Engineers' Society of Western Pennsylvania*, xvii., No. 7.

2nd.—Only one-third as much acid is used as for the lead peroxide method.

3rd.—The small size of the test-tube that may be used—a one inch by eight inch tube replacing a one inch by ten inch tube, previously used, at only one-half the cost.

4th.—As the oxidation takes place below the boiling point of water, a simple water-bath can be used for the entire operation, thereby doing away with the heating over an argand burner, or hot plate, or the use of a calcium chloride bath, with the result that the breakage due to these higher temperatures is considerably reduced.

5th.—It is neater, quicker, and fully as accurate.

The use of the silver salt does not create much expense, as one grm. will make fifty determinations. The present price of the ammonium persulphate is $1.00 per pound; in ten pound lots or more, 85 cents per pound. If the use of this method should become extensive, thereby creating a demand for the salt, it is reasonable to suppose that these prices would be greatly reduced. The comparative cost per hundred determinations, using the quotations of a local supply house, would be:—

Ammonium persulphate method ..	33·8 cents
Lead peroxide method	50·8 ,,

Using the quotations obtained by one of the mill laboratories the cost would be:—

Ammonium persulphate method ..	20·9 cents
Lead peroxide method	38·3 ,,

In conclusion, I would say that the method has been in use for some time at the laboratory of the Duquesne Steel Works and Blast Furnaces, and has given perfect satisfaction for all ranges of manganese.

The persulphate is also an excellent substitute for bromide in the oxidation of manganese in alkaline solutions. It has been found good practice to add the salt direct to the boiling solutions.

I also wish to acknowledge my thanks to Mr. J. M. Camp, chief chemist at the Duquesne laboratory, for many valuable suggestions in the writing of this paper.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, November 8th, 1901.

Mr. T. H. Blakesley, Vice-President, in the Chair.

A Paper on "*A Voltameter for Small Currents*" was read by Dr. R. A. Lehfeldt.

The instrument consists of a capillary tube about 25 c.m. long, completely filled with mercury, with the exception of a bubble of mercurous nitrate solution, about 1 c.m. long, placed near the middle of the tube. Connection with the two mercury columns is made by means of platinum wires passing through the side of the tube. To use the instrument it is placed in a vertical position, the anode being at the top, and the quantity of electricity which passes through is measured by the change in volume of either electrode. In a test experiment the change in volume was measured by means of a micrometer, and agreed within 0·6 per cent with the amount deduced from the known value of the current. It is necessary that the currents should be small so as to avoid complications due to polarisation.

The Chairman pointed out that the presence of air in the tube would render the readings inaccurate, and asked if it was necessary to apply any temperature correction.

Dr. Lehfeldt said that it was quite easy to seal the tube without admitting air, and the temperature correction was negligible.

A "*Note on a Paper by Prof. Fleming and Mr. Ashton entitled 'On a Model which Imitates the Behaviour of Dielectrics,*'" by Dr. J. Buchanan, was read by the Secretary.

The action of this model depends on the viscosity of a liquid, and the diagrams derived from it show by their form that the motion of the pencil which traced them approximated closely to what may be expressed by the term "motion of a viscous fluid by diffusion." In other words, the displacement curves obtained from the model, and their derived velocity curves, are of the same form as the graphs of certain solutions of Fourier's well-known equation $\frac{dv}{dt} = K\frac{d^2v}{dx^2}$. Lord Kelvin has shown that the potential and the current at any point in the wire of a cable can be expressed by appropriate solutions of this equation, and in the same manner by the use of solutions of this equation the diffusion of electricity into or out of the dielectric of a condenser can be treated. It appears, therefore, that the motion of the model and the diffusion of electricity in a dielectric are subject to one and the same mathematical law. The author suggests that the inventors should obtain hysteresis diagrams by cyclical loading of the springs.

Prof. J. A. Fleming said he was glad that Dr. Buchanan had drawn attention again to the model, because there were points about it which might be amplified with advantage. After giving a short description of the apparatus, he said that Dr. Buchanan had shown that mathematically the theory of the model was the same as that of diffusion in a cable, and he suggested that there might be something more than mathematical analogy. Prof. Fleming referred to the discussion on the original paper, in which Prof. Ayrton asked in what respect the model served its purpose better than a twisted wire. A twisted wire cannot represent the properties of a dielectric, because if twisted beyond the elastic limits there is a permanent set. There is no permanent set in the present model. He would like to know if a dielectric has a true conductivity, and suggested that experiments should be made by subjecting a dielectric to constant electric pressure at constant temperature, for years if necessary, and observing whether the curve of current becomes asymptotic to the zero line, or to a line parallel to it. The model could be made to represent a conduction as well as a displacement current by so arranging the bottom piston that it could descend but not return. The fact that the movements of the model were similar to the diffusion of current in a cable suggested that the process of conduction in a metal was similar to that of displacement in a dielectric.

Mr. J. Macfarlane Gray read a "*Note on the Numerical Value of the 'Characteristic' of Water.*"

The author referred to a paper on theormodynamics which he wrote twenty years ago, and in which he supported the theory of a granular ether under enormous pressure. This theory easily explains the properties of bodies. There is a numerical characteristic for every substance in the state of vapour. This characteristic can be deduced from an analytical expression involving certain physical data which must be experimentally determined. His original number for water was 25·30693, but later experiments by Lord Rayleigh on the weight of hydrogen have altered this number to 25·33776. The author's original value for the absolute specific heat of water was 1·4960 "m.m. lift at Paris," but recent experiments of Callendar give 1·26230. According to the author's theory, water commences to freeze at 95° F., and the variation of the specific heat of water at low temperatures is due to the latent heat of ice. The formation of ice particles also explains the peculiar changes in volume of water as it cools to the freezing-point.

The Chairman asked if this theory could explain the fact that water can remain liquid below 32° F.

Mr. Macfarlane Gray said it could.

The Society then adjourned until November 22nd, 1901.

NOTICES OF BOOKS.

The Cost of Food; a Study in Dietaries. By Ellen H. Richards. New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1901. 12mo. Pp. 161.

The previous works by Mrs. Richards, "The Cost of Living as Modified by Sanitary Science," "Food Materials and their Adulterations," "Air, Water, and Food," together with the one under review, combine to establish her as an earnest student of the controlling factor in all life-food supply, and competent to give publicity to her theories as well as to make known the facts she so laboriously collects.

In successive chapters are discussed the kind, quality, and cost of food required and suited to infants, children at school, active youth, college students, brain workers, travelling and professional men, as well as persons in pauper and penal institutions, and hospitals. Subjects further dwelt upon are the general principles governing dietaries and lists of dietaries, with the exact cost per day per person. A very useful glossary of terms and a bibliography of the recent literature close the carefully prepared volume.

The author endeavours to show the relative cost of the right amount of the food-stuffs when derived from the various food materials. She recognises that this is largely influenced by the preparation and combination to which the food is subjected outside the body, as well as by the "mental and physical condition of the body receiving" it.

The author condemns the intemperance and wastefulness in food so very common in the United States, and uses the following language with regard to indulging children.—

"It is also true that a taste for highly spiced food, for sweets, &c., may be fixed by a very little unwise indulgence, especially since habit rather than instinct guides civilised man in the choice of food. It is the first taste that costs; no sane mother would give her child coffee or wine; why should she yield to its curiosity and give spiced foods and rich gravies? If the child is not taught to be whimsical and fickle in appetite, he will rarely make any remarks about his food. Alas, he usually hears too much for and against food, and as the parrot's vocabulary betrays his ship companions, so the child's fancies betray his parents and nurse."

The prices given for the various kinds of food are much cheaper than any with which the reviewer is acquainted; the author estimates, for example, the cost of coffee, milk, and sugar for six persons at one meal at twopence halfpenny!

In an interesting chapter the author explains the process by which the dietaries have been computed. There is an index.

Recherches Rétrospectives sur l'Art de la Distillation. Historique de l'Alcool de l'Alambic et de l'Alcoométrie. By J. Dujardin. Paris: chez l'Auteur, 24, Rue Pavée. 1900. Pp. xvi.—236. 8vo. 125 Illustratione.

Besides the topics named in the title, this richly illustrated book treats of the history of wine, of the origin of alcohol, and of the knowledge of the alchemists concerning the operation of distilling, as well as the methods and apparatus used in later times. It is made up chiefly of extracts from unusual books and authors, arranged chronologically with a thread supplied by the compiler. Prominent are the works of Berthelot (with reference to the Greek and Arabian sources), Gesner, Brunswich, Agricola, Lemery, Barlet, Glauber, and others.

This method of compilation gives the book at first sight a disjointed look, but the reader must note that the author states in his preface that he has not prepared a scientific study, but simply a "pictorial and bibliographic history of alcohol and of the alembic." And as respects the reproductions of engravings the book is eminently attractive, but the bibliographic part is insufficient; the data are not full, except in a few instances, the place of publication being generally omitted. The sources of the engravings are usually mentioned, but that of the very first plate (opposite page 2) is lacking. Again, the bibliographic data of a given book are not always given in the same order. (See Barlet, pages 91 and 116).

An interesting feature is the reproduction of entire pages of rare books, showing quaint typography and cuts. The author spent fifteen years collecting the material for this volume, and is to be congratulated on the result.

Unfortunately, there is no list of illustrations, and no index of subjects; merely an index of proper names.

The reviewer is tempted to transcribe the following short legend of Arabic origin which he recognises as a variant of the Talmudic version: "When Noah had planted a vineyard, Satan came and watered it with the blood of a peacock; when the leaves began to grow, he sprinkled it with the blood of a monkey; when the young fruit appeared, he used the blood of a lion; and when the bunches of grapes were quite ripe, he used the blood of a hog. The vines watered with the blood of these four animals acquired different characters. When the wine-drinker sips his first glass of wine, he becomes animated and vivacious, his colours become more gaudy, he acquires at this stage the brilliancy of a peacock; when the fumes of wine begin to affect his head, he becomes gay and he acts like a monkey; when thoroughly intoxicated with more drink, he becomes furious like a lion, and finally he lies down, stretches out to sleep, and behaves like a hog."

H. C. B.

Memorial Lectures delivered before the Chemical Society, 1893—1900. London: Gurney and Jackson. 1901.

The thanks of all chemists are due to the Council of the Chemical Society for the publication of the valuable book now before us.

As is well known it has been the custom for some years past for the Chemical Society to commemorate deceased Foreign Chemists on its roll of Honorary and Foreign Members by a Memorial Lecture devoted to an account of their life and work. In every case care has been taken to select as the Lecturer some well-known chemist who by his intimacy with, and knowledge of, the special subjects to which the deceased *savant* had devoted his time, was peculiarly fitted to deal with such subject.

These lectures were originally published in the Society's Journal, but they will naturally be more available to the reading public in the form in which they now appear.

Besides giving an authoritative account of the genesis and development of most of the theories which lie at the root of modern Chemical Science, the lectures are in many cases themselves important contributions to science.

Without wishing to make invidious distinctions, we may mention the Helmholtz Lecture, by the late Prof. Fitzgerald; the Pasteur Lecture, by Prof. Frankland; and the Kekulé Lecture, by Prof. Japp, as being of special interest and importance.

With each lecture there is an excellent portrait of the chemist with which that lecture deals, and the whole forms a volume which should be found in every good library.

A Manual of Determinative Bacteriology. By Frederick D. Chester. London: Macmillan and Co., Limited. New York: The Macmillan Company. 1901. Pp. 401.

The author undertook the important labour of arranging the several hundred bacteria which are known to science in such a manner that it would be more easy to identify any particular one, or at any rate, to determine whether it was already known or not. The amount of work involved in performing this task has been necessarily very

considerable, and the results are now embodied in the present volume.

The hope is expressed that by using this book as a laboratory manual the student will be able to identify a given culture, as is done with other organic bodies, without the expenditure of that great amount of labour which has made the identification of many microbes so serious a matter as to become almost impracticable.

The general scheme for the study of bacteria is given in Chapter II., on page 41, and is closely followed in Chapter III. by the classification of bacteria. In this chapter they are divided up, and arranged in various groups, according to their different properties, in a similar manner to the well-known analytical tables used for inorganic analysis, only in the present case the subject is a much more complicated one, and many more characteristics have to be sought after and confirmed, while the number of separate microbes is counted by hundreds. Following these tables, which occupy practically the whole book, we find a glossary of the terms used in descriptive bacteriology, a most useful adjunct to this comparatively new and complicated science.

The author has given us a valuable work which will be of great help to bacteriologists.

The Gas Engineer's Pocket-Book. Comprising Tables Notes, and Memoranda relating to the Manufacture, Distribution, and Use of Coal-gas, and the Construction of Gas Works. By HENRY O'CONNOR. Second Edition, Revised. London: Crosby Lockwood and Son. 1901. Pp. 454.

THAT this pocket-book has fulfilled its promise is shown by the necessity for a second edition. We have little to add to our remarks concerning the first edition, save that its usefulness is evidenced by its success. A few errors of the press have been corrected; the Statutory regulations for testing the illumination power and purity of gas have been added, and the text of the book amended where it was found advisable.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 17, October 21, 1901.

The Limit of Chemical Reactions and that of the Product PV in Gases.—A. Ponsot.—The two hypotheses—"PV tends towards a limiting value when V becomes infinite," and "there are complete chemical reactions,"—are incompatible. However, the two hypotheses —"PV tends towards a limiting value for an infinite value of V," and "Chemical reactions are always limited," —are compatible; also the two hypotheses—"P=o for very large values for V," and "There are complete chemical reactions and also limited chemical reactions."

Action of Pyridic Bases on the Tetrahalogen Quinones. Hydroquinonic Derivatives. — Henri Imbert.— The author recently intimated that pyridic bases, of which the two α-positions are free, react on chloranile and bromanile, producing bodies having the constitution $R.C_5H_3N—C_6X_2O_2—OH$ or $_{OH}^{R}>C_5HN=C_6X_2O_2$.

These products, under the influence of bases, easily lose a halogen atom, which is replaced by OM' (M' being a monovalent metal). Acids set free a red body having the formula $R.C_5H_3N—C_6X(OH)O_2—OH$, assuming the pyridic formula, which is the most probable. In the present research, the author assures himself that the quinonic function really persists in the molecule by reducing the body: $—C_5H_4N—C_6Cl_2O_2—(OH)$.

Oxidation of Benzenic Carbides by means of Manganese Dioxide and Sulphuric Acid.—H. Fournier.—The author examines the method of oxidation of various homologues of benzene by means of manganese dioxide and sulphuric acid. In the case of orthoxylene, he obtains a yield of *o*-toluic aldehyde of 37 per cent. Oxidation of pseudocumene by this method gives a yield of 22 per cent of aldehyde. In the case of paracymene, a very small quantity of aldehyde is produced.

Action of Ammonia on Benzyl Chloride, and Conditions of Formation of Benzylamine.—René D'hommée.—The reaction of ammonia on an halogenated ether usually gives a primary amine salt, with small quantities of secondary and tertiary salts of this alkali. Under certain circumstances, however, these latter predominate. The author examines the conditions which determine the course of these reactions, and he finds that in all his experiments benzylamine is chiefly produced in presence of a large excess of ammonia. The yield was as much as 44·5 per cent of benzyl chloride. To prepare the benzylamine in tolerably large quantity a yield of 42·6 per cent is best.

The Amine Derivative of the supposed Binaphthylene Glycol.—R. Fosse.—The amine which can be derived from the supposed binaphthylene glycol, and to which the formula $\begin{matrix} C_{10}H_6—C—OH \\ | \quad\quad || \\ C_{10}H_6—C—NH_2 \end{matrix}$ has been attributed, is in reality a derivative of dinaphthoxanthene, and possesses the formula $O<_{C_{10}H_6}^{C_{10}H_6}>CH—NH—CH<_{C_{10}H_6}^{C_{10}H_6}>O$. This is the bis-dinaphthoxanthene amine. Fuming hydracids do not transform this amine into its salts, but decompose it into NH_4Cl or NH_4Br and mono-, chloro-, or bromo-dinaphthoxanthene, $X—CH<_{C_{10}H_6}^{C_{10}H_6}>O$. A solution of the amine in the hydracids added to $PtCl_4$ gives the chloroplatinate of NH_4 and a double chloride of platinum and dinaphthoxanthene, $PtCl_4+2Cl—CH<_{C_{10}H_6}^{C_{10}H_6}>O$.

Nitrated Derivatives of Arabite and Rhamnite. Constitution of certain Nitric Ethers.—Leo Vignon and F. Gérin.—The authors have already shown that nitric ethers of alcohols with an open chain, whose atomicity is equal or greater than 4, possess reducing properties with regard to cupro-potassic solution. These conclusions are now confirmed by a study of the nitrated derivatives of arabite and rhamnite, and also the authors examine the constitution of the nitric ethers of erythrite, mannite, dulcite, arabite, and rhamnite.

Glycerophosphorous Acid and the Glycerophosphites.—Auguste Lumière, Louis Lumière, and F. Perrin. —Glycerophosphorous acid can be prepared by the action of phosphorus trichloride on glycerin, and from the acid a number of glycerophosphites are obtained. The greater number of these latter are soluble in water. A neutral solution of sodium or ammonium glycerophosphite gives no precipitate with salts of copper, iron, zinc, nickel, lead, mercury, or manganese; but with silver nitrate a white precipitate is obtained, which rapidly darkens. The calcium salt can be prepared in the form of a soluble powder, extremely soluble in water and deliquescent.

Journal de Pharmacie et de Chimie, Series 6, Vol. xiii., No. 8.

Transformation of Creatine into Creatinine by a Soluble Dehydrating Ferment in the Organism.—Er. Gérard.—Already noticed.

Action of the Waters from Sétif on Lead.—Dr. Malmejac.—Numerous analyses have been made from time to time of the waters from Sétif, and these have been very concordant, giving the following results:—

Hardness	24°
Carbonic acid	13 c.c. per litre
Carbonate of lime ..	0·100 grm. ,,
Sulphate of lime.. ..	0·052 ,, ,,
Sulphate of magnesia .	0·110 ,, ,,
Chlorides	traces
Total..	0·262 ,, ,,

Three samples, of 100 grms. each, of this water were placed in glass vessels and left in free contact with the air. In the first, a strip of lead weighing 15 grms. was placed; in the second, a similar strip of lead fastened to an iron wire, which was also in the water; in the third, another similar strip of lead surrounded with copper filings. These were left for twenty days, when the following losses of weight were found to have taken place:—

No. 1.	0·02 grm.
,, 2.	0·04 ,,
,, 3.	0·10 ,,

After the first few days, in No. 3 tube a very voluminous precipitate was formed, which far exceeded that formed in either of the two other tubes.

Estimation of the Free Hydrochloric Acid in Gastric Juice.—Dr. Meunier.—In the quantitative estimation of free hydrochloric acid by colorimetric methods, two reagents in particular are used at the present time—that of Toppfer, with dimethylamidoazobenzol; and that of Gunzbourg, with phloroglucine vanilline. The first process is simple to carry out and rapid, but it is not very easy to read the exact change of colour. The other method, however, gives constant results when once sufficient skill has been acquired. The author now proposes a new method, which is a combination of these two, and gets very good results.

No. 9.

On Cinchonine.—E. Jungfleisch and E. Léger.—Already noticed.

Action of Caprylic Alcohol on its Soda Derivative. Synthesis of the Dicaprylic and Tricaprylic Alcohols.—Marcel Guerbet.—Already noticed.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 4th inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair. Mrs. Crowdy was elected a Member.

Formation of Indigo from the Malonic Ether of Anthranilic Acid.—D. Vorlander and C. Koettnitz.—The authors have observed that in the condensation of compounds containing the methine group, concentrated sulphuric acid, contrary to the alkaline methods of condensation, facilitates the elimination of water from the group in question. It is thus that the malonic ether of anthranilic acid,

$$C_6H_4 \begin{cases} NH-CH(COOR)_2 \\ COOH \end{cases},$$

and some other similar compounds are changed, when heated with concentrated sulphuric acid, into indigo-sulphonic acids. To prepare the diethylic ether from the tribasic acid, anthranilic acid is heated to gentle boiling for about three-quarters of an hour with the diethylic ether of mono-bromo-malonic acid and water; the ether formed melts at 127°. Its alcoholic solution is coloured a brownish-red by $FeCl_3$. The corresponding acid melts at 185°, and behaves like the ether; with sulphuric acid it gives indigo-disulphonic acid, and by fusion with caustic potash it yields indoxyl or indigo. The neutral ether, fusible at 122—124°, obtained by reacting with bromo-malonic ether on the ethylic ether of anthranilic acid, is not so easily transformed into indigo.—*Berichte*, vol. xxxiii., p. 2466.

Action of Oxygen Gas on Cobalticyanide of Potassium, and on the Chromous Salts.—W. Manchot and J. Herzog.—It is known that a solution of cobalticyanide of potassium rapidly absorbs oxygen from the air; Zwenger (*Liebig's Ann. Chem.*, vol. lxii., p. 157) gives the reaction $8KCy + 2CoCy_2 + H_2O + O = 2CoCy_6K_3 + 2KOH$. The authors have observed that the volume of oxygen is about double that indicated by the preceding equation, and further, that notable quantities of peroxide of hydrogen are formed. They are of the opinion that this latter body results from the oxidation of the nascent hydrogen at first given off by the cobalticyanide; as a matter of fact, in the absence of air, solutions of $CoCy_6K_4$, when warm and concentrated, give off free hydrogen. This has led them to compare the oxidation of the cobalticyanides with that of the chromous salts; with these latter the absorption of oxygen is much more rapid and the formation of peroxide of hydrogen is not observed; the same is the case with ferrous hydrate. The authors suggest the following experiment with chromous chloride:—A fragment of metallic chromium and some water are placed in a small flask fitted with a funnel furnished with a tap, and an escape tube; boil to drive out the air, then add hydrochloric acid; the chromium dissolves, giving off hydrogen plentifully; when the whole is dissolved, a blue solution remains. If we now continue to boil, small bubbles of hydrogen are given off and the solution becomes green.—*Berichte*, vol. xxxiii., p. 1742.

The Theory of Saponification.—J. Lewkowitsch.—It has been generally imagined that the triglycerides $C_3H_5(OR)_3$ are entirely saponified according to the equation $:-C_3H_5(OR)_3 + 3MOH = C_3H_5(OH)_3 + 3MOR$. There would, consequently, be no intermediate step characterised by the formation of a mono- or di-glyceride. This opinion has recently been challenged by M. Geitel, so the author has decided to settle the question in a definite manner. For this purpose he has made use of the degree of acetylation. This figure should always be nil if the saponification is complete, as the product freed by washings from glycerin and the soap formed would consist of a triglyceride and an acid ROH. It is true that we must not forget the action of acetic anhydride on this latter, an action which gives a small quantity of a mixed anhydride. Now the author has observed that the degree of acetylation is not nil, but that it varies considerably during the progress of saponification. (Naturally the degree of acetylation of the original material must be taken into account). Two other figures, viz., that of Hehner (insoluble acids), and the degree of saponification, were determined concurrently on samples taken after varying periods; these figures differ considerably from the limits corresponding to the acid R.OH, and the triglyceride. The original paper gives a detailed description of the experiments carried out on tallow and cotton-seed oil. As saponifiers, lime and caustic soda were used.—*Berichte*, vol. xxxiii., p. 89.

The Double Metallic Thiocyanates.—A. Rosenheim and R. Cohn.—The following salts have been prepared by the mixing of solutions:—*Bromothiocyanate of Mercury*, $CNS.HgBr$.—It forms beautiful needles, almost insoluble in water, soluble in warm alcohol. *Double Mercuric Thiocyanates.*—There are notably two well-crystallised salts of barium, one of which, $[(CNS)_3Hg]_2Ba$, is slightly soluble, while the other, $(CNS)_4HgBa$, is very soluble; the analogous double salts of NH_4, K, Na, and Cu belong to one or the other of these types. *The Double Thiocyanates of Lead* are analogous to the preceding salts. *Double Thiocyanates of Cobalt.*—These occur as blue crystals, fairly soluble, giving solutions which are

blue when concentrated and rose-coloured when dilute: — $(CNS)_4K_2Co+4H_2O$, $(CNS)_4Na_2Co+8H_2O$, $(CNS)_4(NH_4)_2Co+4H_2O$, $(CNS)_4B_4Co+8H_2O$. *Double Thiocyanates of Nickel.*—These occur as green crystals, very soluble in water, slightly soluble in alcohol, $(CNS)_4Na_2Ni+8H_2O$ and $(CNS)_6K_4Ni+8H_2O$. The *Double Thiocyanates of Aluminium or of Chromium* crystallise from a syrupy solution, $(CNS)_6K_3Al+4H_2O$ and $(CNS)_6K_3Cr+4H_2O$.—*Berichte*, vol. xxxiii., p. 1111.

Iodide of Nitrogen, N_3I.—A. Hantzsch.—Iodine reacts on nitride of silver, N_3Ag, giving rise to a new iodide of nitrogen, N_3I, which, in certain of its properties, resembles iodide of cyanogen. To prepare this body we shake up an aqueous emulsion of nitride of silver with a benzenic or ethereal solution of iodine (about one atom per molecule). The temperature must be kept down to 0°. We then decant the faintly yellow ethereal solution, dry over anhydrous sulphate of soda, and drive off the ether with a current of air, avoiding all traces of moisture and any elevation of temperature. The yellowish residue is washed with ligroïn to remove the iodine, and more or less pure N_3I is left. This iodide is soluble in water, it has a piquant smell, and reacts on nitrate of silver in the following manner:—

$$N_3I+2AgNO_3+H_2O=AgN_3+AgOI+2NO_3H,$$
$$3AgOI=2AgI+AgIO_3.$$

The precipitate of iodide, iodate, and nitride is heated with dilute sulphuric acid, the hydronitric acid distilled over is titrated with decinormal nitrate of silver. The residue is treated with iodide of potassium, and the iodine set free is titrated with hyposulphite; this method has enabled us to ascertain the exact composition of the iodide of nitrogen. This iodide detonates even more easily than the iodides already known; it is soluble in most organic solvents, but the solutions formed gradually decompose with the evolution of nitrogen; the aqueous solution is neutral to litmus, and does not act on starch-paste. It decomposes according to the two following equations: $-2N_3I=3N_2+I_2$. $5N_3I+3H_2O=5N_3H+HIO_3+2I_2$. Alkalis act in the same manner.—*Berichte*, vol. xxxiii., p. 522.

MEETINGS FOR THE WEEK.

Wednesday, 20th.—Microscopical, 7.30. An Exhibition of "Some Antipoints seen under the Microscope," by Conrad Beck. "On Stereomicrography," by Prof. G. P. Girdwood.

—— Society of Arts, 8. Opening Address of the 148th Session, by Sir W. H. Preece, F.R.S., &c.

Thursday, 21st.—Chemical, 8. "On the Oxidation of Sulphurous Acid to Dithionic Acid by Metallic Oxides," by H. C. H. Carpenter. "Optically Active β-Hydroxybutyric Acids," by A. McKenzie. "On the Hydrochloride of Thiocarbamide," by H. P. Stevens. "The Constituents of the Essential Oil of Asarum Canadense," by F. B. Power and F. H. Lees. "Note on the Reduction of Trinitrobenzene and Trinitrotoluene with Hydrogen Sulphide," by J. B. Cohen and H. D. Dakin.

Friday, 22nd.—Physical, 5. "Multiple Transmission Fixed Arm Spectroscopes" and "On the Measurement of Young's Modulus," by Prof. W. Cassie. "Notes on Gas Thermometry—Part II.," by Dr. P. Chappuis.

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THE CHEMICAL NEWS.

Vol. LXXXIV., No. 2191.

THE PLACE OF THE RARE EARTH METALS AMONG THE ELEMENTS.

By B. D. STEELE, B.Sc. (Melbourne).

The generally accepted classifications of the chemical elements, all of which are modifications of those first proposed by Mendeleeff and Lothar Meyer, are open to a common objection, in that they fail to assign any place to the metals of the rare earths. Many attempts have been made to assign to certain of these elements a position in one or other of the groups, and quite recently Brauner (*C. C.*, 1900, II., 524) has endeavoured to show that Prd may be placed in the fifth group and Nd in the sixth, since Prd forms an oxide, Prd_2O_5, and he thinks that perfectly pure Nd would form an oxide, Nd_2O_6 (*C. C.*, 1898, I., 919).

such modification results in an increased power of generalisation and prediction.

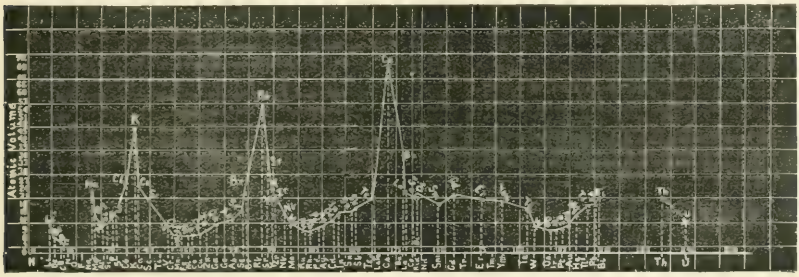
In addition to the three elements predicted by Mendeleeff in 1869, and since discovered in Sc, Ga, and Ge, no less that fifteen new elements are indicated by the law in its present form as existing with atomic weights lying between those of Ce = 140 and Ta = 183, these being necessary to complete Mendeleeff's eighth, ninth, and tenth series. A considerable number of elements are known (the rare earth elements), which have these atomic weights assigned to them, but their properties are such that they require all to be placed in one, the third, group instead of being distributed through seven.

Julius Thomsen (*Zeit. fur Anorg. Chemie*), 1895, ix, p. 190) has suggested a classification whose essential features are the recognition of three chief groups of elements; the first containing two smaller groups of seven each, the second containing two groups of seventeen elements, and the third containing one, and probably two groups, of thirty-one elements each.

It has been generally taken for granted that if the gap between Ce and Ta were filled up we should have Mendeleeff's eighth and tenth even, and ninth uneven series completed.

Lothar Meyer supposed that his curve when completed would repeat in this section the periodicity so clearly

Fig. 1.



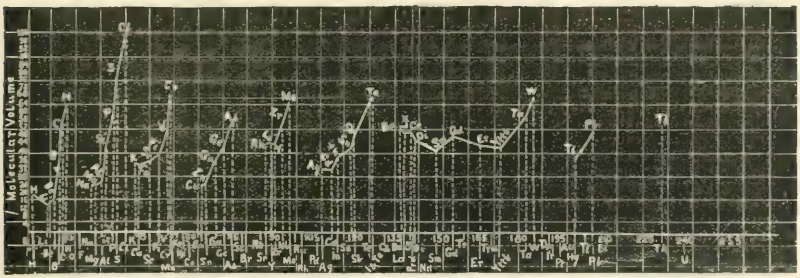


Fig. 2.

Such a mode of explaining the difficulty, however, does not seem to be consistent with a consideration of all the properties of the compounds of these elements.

Since the periodic law is an empirical law and is only an expression and classification of facts, by the aid of which it is possible to make predictions concerning the properties of discovered and the existence of undiscovered elements, we are justified in taking another and different course, that of modifying the form of the law, provided

shown in the other portions, and quite recently Stefan Meyer (*Monatsh. f. Chem.*, xx., 269), when comparing the atomic volume and the atomic magnetism, assumes the extension of the periodicity to this portion of the table.

It is a fact that no instance is known in which two elements of distinctly different properties occupy the same position in the periodic system, which would be the case if, for instance, ytterbium had assigned to it an atomic

weight $\frac{173}{3}$ or $173 \times \frac{2}{3}$; in the former case it would fall between Fe and Ni, in the latter between In and Sn. On the other hand, no elements other than the rare earth metals are known which occupy any position between Ce and Ta.

The question, however, arises as to whether the atomic weights usually given to these elements are the correct ones. That this is so is very probable, although this constant cannot be determined with as much certainty for these as for the other elements.

The recent investigations on "Magnetic Susceptibility," by Stefan Meyer (*loc. cit.*), and Du Bois and Liebknecht (*Ber.*, 1899, xxxii., 3344) have shown that in the series of the elements the atomic magnetic susceptibility of the element or the molecular magnetic susceptibility of the oxides reaches a maximum (paramagnetic) in two series of elements; the first being the series Cr—Co, the other being the group of rare earths

In the series Ba, La, Ce, Prd, Nd, Sm, Gd, Er, Yb, Ta, the oxides pass from diamagnetism to paramagnetism between Ba and Ta, the paramagnetism rises rapidly through Ce, &c., to a maximum at Er, falling again through Yb, Ta being again diamagnetic, and throughout this series the susceptibility is much greater than anywhere else except in the iron group. From this and from a consideration of all the properties of these elements it seems that, whatever their atomic weights may be, they at least lie close together, and are arranged in their proper order. If therefore we can determine the atomic weight of one of these elements more certainty will be attached to those of the whole series.

From Nilson's (*Ber.*, xiii., 1433) determination of the specific heat of Yb_2O_3 it is possible to approximately calculate the atomic weight of Yb.

Assuming the atomic heat of oxygen to be 4, the atomic weight of Yb is thus found to be 164, which is sufficiently near the accepted number 173.

The only compound which exists for all the rare earths whose properties may be compared with the corresponding compound of the other elements is the oxide; and here the difficulty arises that we have to compare oxides of different types for different elements. Mendeleeff, however, has pointed out that if we consider the molecular volume of the typical salt forming oxides, a periodic variation is found to exist. No difficulty arises in the choice of oxide for the rare earths, since, in the majority of cases, only one is known to exist; exceptions being Ce, Prd, and Nd. For the two latter no data are available, and in what follows, therefore, the molecular volume of Di_2O_3 is considered, and no radical difference is observed if Di_2O_5 is taken for comparison instead.

By plotting the molecular volume of the oxide against the atomic weight of the element Curve I. is obtained, and it will be seen that the region of the curve under discussion is horizontal, and the periodicity so clearly shown in other parts is not reproduced.

Unfortunately, data do not yet exist* for the completion of Lothar Meyer's curve of atomic volumes. Nevertheless, it is possible to calculate approximately the atomic volume from the molecular volume of the oxides.

The molecular volume of an oxide is not an additive property, since it is found that in the conversion of an element into its oxide very different volume changes take place according to the chemical properties of the element in question. Thus, for the strong alkalis and alkaline earths, the atomic volume of the oxygen in the oxide has a negative value, in acid oxides it has its greatest positive value; whilst for intermediate oxides and such as have only a slight tendency towards the formation of salts, the change in volume is least, and is nearly equal to zero.

This is clearly shown in the series of elements:—

	Na.	Mg.	Al.	Si.	P.	S.	Cl.	K.
A. V. ..	23·7	13·8	10·6	11·2	13·5	15·7	25·6	45·4
M. V. oxide	12	11·5	13	22·5	30	41	48	17
Vol. of O..	−22	−4·5	+1·4	+5·2	+6·2	+8·7	+6	−35

In addition, the volume of the oxygen is—

$ZrO_2 = 0$, $La_2O_3 = +1$, $Ce_2O_2 = +2$, $ThO_2 + 2$.

If therefore we assume for an approximation that the volume of the O in the rare earth oxides = 1·5, and then calculate the volumes of the elements, we may complete Lothar Meyer's curve. In this manner Curve II. is obtained, in which, as in Curve I., we see that the rare earths show no tendency to repeat the periodicity of the other portions.

The value for atomic volume has also been calculated for Sc, Y, La, Ce, Di, and the values so found show a very close agreement with the experimental figures.

As has already been mentioned, the figures for Di have been employed, as the density of Prd and Nd has not yet been determined.

Other properties of these compounds point also to the fact that the atomic volumes are not large. Thus, Stefan Meyer has shown that the elements with large atomic volumes are diamagnetic, whilst, on the other hand, the paramagnetic elements have small atomic volumes.

Similarly, Abegg and Bodländer (*Zeit. Anorg. Chemie*, 1899, xx., 453) have shown that the tendency towards the formation of ions is conditioned by the atomic volume; this tendency being much less with those elements which possess a small atomic volume.

From the preceding, the conclusion is drawn that the periodicity of the elements is such that there exist—First, two series of seven elements each. These are followed by a second two series of seventeen elements each, in each of which the first and the last seven repeat to a greater or less extent the properties of the first two series; the three intermediate elements in each long series forming an interperiodic gronp. Just as the periodicity of the first two series undergoes a change on passing to the third (long) series, so the fourth (long) series again undergoes a change in the form of periodicity on passing to the next series; the change being in this case again brought about by the introduction of what may be termed an interperiodic group—the group of the rare earth metals, which have several characteristics in common with the elements of the eighth (interperiodic) group. Thus the individual members are separated from one another only with the greatest difficulty, they occur together in nature, have very nearly the same atomic volume, and possess strongly marked paramagnetic properties.

The next series differs again from this in its periodicity. At present only two elements, Th and U, in this series are known to exist with absolute certainty; but, from the difference in atomic weight between Bi (the last known member of the preceding series) and U (which undoubtedly is correctly placed in the sixth group), it is evident that no series of elements will be found to exist in this position corresponding in place and properties to the rare earth elements.

The advantages that may be expected from a modification of the law in this direction are two:—Firstly, the clearing away of much confusion; and, secondly, an increased power of generalisation and anticipation. Thus, it is at once evident that the number of undiscovered elements is considerably reduced, the fifth and sixth groups being completed as far as Ta and Bi in the one case, and U and Te in the other. On the other hand, the fact that elements are lacking in the seventh group below Mn becomes more emphasised, as is also the case with the missing homologues of Te and I.

Moreover, should a further homologue of K be discovered, it will be found to have an atomic weight of about 218, and not 172. Such an element would occur in the same series with the well-known elements Th and U, in which are also probably the more doubtful elements

* Stefan Meyer (*Monatsh. fur Chemie*, xx., 793) has determined the atomic volume of erbium, but says nothing about the purity or mode of preparation of the specimen of metal employed; it was obtained from Merck, and was probably very impure; it had a density 4·77, atomic volume = 34·9.

radium and polonium, which have been recently discovered. That radium has a very high atomic weight is shown by S. Curie (*Comptes Rendus*, 1900, cxxxi., 382; CHEMICAL NEWS, vol. lxxxi., p. 98), who states that the atomic weight must be much greater than 174.

It is probable—since these two elements, in common with Th and U, are characterised by the possession of radio-activity—that this will be found to be a property peculiar to the elements of very high atomic weight, and that the occasional occurrence of this property in elements of lower atomic weight, *e.g.*, Ba, Y, Bi, &c., may ultimately be traced to admixture of minute traces of elements belonging to this series.

VOLUMETRIC ESTIMATION OF MANGANESE.

By FRED. IBBOTSON and HARRY BREARLEY.

WE are very pleased to note Mr. Ramage's amended description of the "bismuthate" process for the estimation of manganese in steel works' materials. There is probably no better volumetric process known for the estimation of both large and small amounts of manganese, and none less subject to the interference of uncommon elements than this may be when suitably modified. On this account we wish to extend the usefulness of Ramage's paper by pointing out some sources of error which have escaped his consideration, and some improvement, as we think, in the general application of the process.

Amongst our friends, and by correspondence with Mr. Ramage, we have attempted during the past two years to determine—(1) Which of the two processes described in Reddrop and Ramage's original paper gave the correct result? (2) why the results differed? and (3) some modification of the operations which should be indifferent to this discrepancy, and which should be as little as possible interfered with by the presence of those elements which occur occasionally in steel.

With respect to the first point, "Is the correct result btained by filtering the oxidised (permanganate) solution into an empty flask and then adding hydrogen peroxide, or into a flask which contains an excess of peroxide to begin with?" We are gratified to find that Ramage has finally come to support our conclusion, viz., that the permanganate should be filtered into an empty flask. But we cannot accept his explanation that, in the original paper, the method of filtering into an empty flask was suggested as an alternative "because we could not be sure of adding *a slight excess* of hydrogen peroxide to the flask before filtration." At that time Reddrop and Ramage appear to have been unaware that an excess of peroxide, either slight or considerable, suffered any deterioration when the oxidised solution was filtered into it. In fact, in a footnote (*Journ. Chem. Soc.*, 1895, lxvii., 275) they say "the large quantity of ferric nitrate in the filtrate tends to the decomposition both of permanganic acid and hydrogen peroxide, the latter less than the former." Ramage's paper (CHEM. NEWS, lxxxiv., 209) makes it plain that the statement in this footnote is untrue, and this puts an entirely different complexion on their original paper, more particularly on the comparison they make between Schneider's process for the volumetric estimation of manganese and their own, which is a modification of it.

The different results obtained by filtering into an empty flask, or into an excess of hydrogen peroxide, are properly explained by Ramage to be due to some reaction between ferric nitrate and the peroxide of hydrogen. Nearly a year ago we observed that if the hydrogen peroxide was standardised by adding it to the solution of a steel which had been used for estimating the manganese, the value of the standard was much lower than if it had been titrated alone or in acidulated water; and, in addition to this, the conclusion that the ferric nitrate destroyed a portion of the hydrogen peroxide was supported by numerous series of tests made on the same steel after adding varying steel amounts of peroxide. One series may be given; it will be seen to agree with Ramage's statement that each c.c. hydrogen peroxide in excess of that really needed corresponds to an error of about 0·01 per cent Mn. The steel used contained 0·32 per cent Mn:—

N/10 H_2O_2 added.	N/10 $KMnO_4$ used.	Per cent Mn registered.
3·95	0·60	0·335
6·75	3·20	0·355
11·60	7·60	0·400
18·60	14·10	0·450

To us a defect of this kind in a reagent suggests the advisability of replacing it by some other. But Ramage sticks to the peroxide and minimises the associated error by adding it in small excess only, and depends upon "a slight reduction of the permanganic acid which takes place during and after filtration" to do the rest. The reduction referred to is undoubtedly due to the carbon of the metal having been but incompletely oxidised by the bismuthate in the cold solution; and in very high carbon steels these intermediate oxidation products of the carbon are revealed as a pronounced yellow colour in the filtered solution after an excess of hydrogen peroxide has been added. In such cases the titration with permanganate may be quite unsatisfactory in that the pink colour, on which the end reaction depends, is discharged almost immediately for an indefinite period. This makes it essential to complete the oxidation of the carbon in hot solutions, for high carbon steels at any rate.

In its application to some steel making alloys, and to steels and irons which contain rare elements, but not so rare as to be above notice, the bismuthate process, if hydrogen peroxide is used, either breaks down altogether or does not work very smoothly. We will consider separately steels or alloys which contain chromium, tungsten, molybdenum, titanium, and vanadium.

Chromium.—In the original paper Reddrop and Ramage observe that bismuthate, when added to a nitric acid solution of a chromium salt, very slowly but completely oxidises it to chromic acid. This oxidation is, happily, so slow in cold solutions that all the manganese may be transformed to permanganate without any appreciable amount of chromic acid being formed. Thus a steel containing 0·50 per cent manganese was dissolved along with 14 c.c. N/10 $K_2Cr_2O_7$. On adding bismuthate, shaking, and at once filtering rapidly, it gave 0·52 per cent Mn; on merely passing the unoxidised solution through a filter already well coated with bismuthate, it gave 0·53 per cent Mn; after standing in contact with bismuthate for five minutes 0·55 per cent Mn, and after ten minutes 0·57 per cent Mn. A long series of steels which have been assayed in other ways also shows that if the solution is kept quite cold the presence of chromium introduces no error unless the contact with bismuthate is extended. Chromium steels which are not completely decomposed by nitric acid are generally got into solution by treating them in the first case with dilute sulphuric, and then adding nitric acid.

Tungsten.—The presence of this element introduces no error; but in steels containing much tungsten, and particularly in chrome-tungsten steels, the precipitate has a tendency to pass the filter. The joint presence of tungsten and hydrofluoric acid (as when ferro-tungstens are opened up with $HF+HNO_3$) cause the results to be high and very erratic; it is necessary in such cases either to drive off the HF with H_2SO_4, or if the manganese is low to adopt the red-lead process (CHEM. NEWS, lxxxii., 209).

Molybdenum.—The presence of this element causes the results to be high and erratic.

Titanium and Vanadium.—The use of hydrogen peroxide has this advantage:—A steel or iron containing titanium or vanadium would be distinguished by the characteristic yellow or reddish-brown colour formed on adding an excess of the peroxide. But the disadvantage of its use under the same circumstances may be twofold:—

1. The oxidised titanium or vanadium compound to which the colour is due does not react so readily

with permanganate as hydrogen peroxide does; so that unless the hot solution is treated with bismuthate or by some other means the colour due to organic matter is destroyed, and the end reaction sharpened, there is some uncertainty about hitting the final point. Otherwise the permanganate reacts with the coloured metallic compounds to the same extent as it would with the hydrogen peroxide which formed them., *i.e.*, the difficulty is one of manipulation merely.

2. When much of either vanadium or titanium is present, as in the assay of their ferro alloys, so deep a colour is formed with the hydrogen peroxide that "a slight excess" over and above that needed to destroy the permanganate cannot be gauged, and thus one is prone to commit the very error which Ramage's paper is intended to eliminate.

We work the bismuthate process as follows:—Dissolve 1·1 grms. of the metal in 35 c.c. of 1·20 nitric acid, and then add bismuthate a little at a time to the somewhat cooled solution until a permanganate colour persists, or on boiling is decomposed to manganic oxide. Clear up the permanganate or the dioxide precipitate with a little hydrogen peroxide, sulphurous acid, or ferrous sulphate, free from manganese. Now cool the solution, and add about 10 c.c. of water, and as much bismuthate as leaves a considerable portion undecomposed. Filter into a clean flask, wash with dilute (3 or 4 per cent) nitric acid, add an excess of ferrous ammonium sulphate, and titrate with decinormal permanganate.

The advantages of using ferrous sulphate are that it does not matter how small or great an excess is added since it does not react with the ferric nitrate, and it can be safely used in cold nitric acid solutions of the above strength if the permanganate titration is not needlessly delayed. In the presence of chromium or tungsten this modification of the process is subject to such limitations as apply when hydrogen peroxide is used, but molybdenum, titanium, and vanadium do not interfere. The only indication during the titration that any of these elements are present is noticed with vanadium; then on adding an excess of ferrous sulphate the blue colour of hypovanadate appears if enough (about 0·5 per cent) vanadium happens to be present. When the excess of ferrous sulphate has been decomposed, and the added permanganate is re-oxidised from V_2O_4 to V_2O_5, the reaction is slower and the end point is not so sharp and clear as when vanadium is absent. This uncertainty, however, need never involve more than one, or at most two-tenths, of a c.c. N/10 permanganate if care has been taken to destroy all the organic matter in the hot solution.

The high price of bismuthate (20s. to 24s. per pound) may retard the general adoption of the process, but it will be found on calculation that this item does not exceed one penny per assay, and is therefore inconsiderable; moreover, the use of 2 grms., as is generally recommended, for the assay of an ordinary steel (particularly if mild) is needlessly extravagant. The economy of the process may be further enhanced when series of everyday steels are being assayed by proceeding as follows:—Pass two or three samples through the same filter; then pour a sample which has been merely dissolved and cooled on to it. A funnel large enough to hold all the ferric solution should be used in order that the bismuthate may be evenly diffused through the liquid by stirring with a glass rod. The filtration should not be accelerated beyond what is necessary to cause the solution to pass rapidly in drops; the results are satisfactory.

By oxidising as usual.	By passing only through filter.
0·62	0·60
2·29	2·25
0·58	0·58
0·68	0·67
0·09	0·10

Bower Road, Sheffield,
November 6, 1901.

VOLUMETRIC ESTIMATION OF MANGANESE.

By LAWRENCE DUFTY.

In a paper on the estimation of manganese by means of "sodium bismuthate," published by Reddrop and Ramage in the *Journ. Chem. Soc.* in 1895, and just recently reviewed by one of the authors in this journal (CHEM. NEWS, lxxxiv., p. 209), a colorimetric method for the estimation of very small amounts of manganese is advocated, a solution of permanganate being used as a standard, and the colours compared in Nessler tubes. No doubt is cast upon the accuracy of results obtained by this process, but in applying it to steel analysis one or two modifications produce a more practical method which works equally well for low and high manganese steels; in addition, as the Mn is determined on the nitric acid solution after estimating carbon by colour, a considerable saving in time (required for weighing out, &c.) is effected.

The modified process is briefly as follows:—The nitric acid solution is transferred (after the carbon has been estimated) to a graduated stoppered test-mixer (on foot); the carbon tube being rinsed out into the mixer, and the solution then made up to a definite volume with nitric acid (HNO_3, sp. gr. 1·20, is used throughout). A standard steel, of known Mn contents, is treated in like manner, being diluted to the same volume as the sample. Equal quantities of "bismuthate" are then added through a dry funnel, and the contents thoroughly mixed; the mixing being repeated five minutes later. After being allowed to settle in a dark cupboard, which usually takes about thirty minutes, measured quantities of the clear pink solutions are transferred by means of a pipette to stoppered carbon tubes, and the colours compared in the usual manner.

In practice it has been found most convenient to weigh out 0·1 grm. of steel, dissolving in 2 or 3 c.c. HNO_3, according to carbon contents, and after the carbon is estimated transferring to 25 c.c. test-mixers, and diluting with HNO_3 to 20 c.c. if the manganese be under 0·8 per cent, or to 25 c.c. if over that percentage. 0·2 grm. "bismuthate" is then added to each tube, and after mixing and allowing to settle, exactly 5 c.c. are transferred to the comparing tubes, the standard being diluted to a convenient tint for comparison (*e.g.*, 0·82 standard to 16·4 c.c.). The standard used for the carbon estimation may conveniently be used for determining the manganese, and one standard solution will serve for a batch of determinations as in colour-carbon.

The question of the varying strength of acid in the mixer affecting the results was investigated, and the following figures show to what extremes the method may be worked. Steel used contained 0·82 per cent Mn. Each sample was dissolved in 3 c.c. HNO_3:—

	Diluted with water to—	Then with HNO_3 (1·20) to—	Result.
	c.c.	c.c.	Mn.
1.	10	25	(Used as standard).
2.	7·5	25	0·82
3.	15·0	25	0·81
4.	25·0	—	0·82
5.	—	25	0·80

The above modification of the "bismuthate process" has been used by the author and others for some time past, and gives every satisfaction. For steel works with Siemens or Bessemer plant, where a large number of analyses have to be made as rapidly as possible, the advantages of this modification over the original volumetric process are obvious; a considerable saving in time not only being effected, but 90 per cent less "bismuthate" is required for each estimation.

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A BIBLIOGRAPHY OF STEEL WORKS ANALYSIS.

Part X.

By HARRY BREARLEY.

(Continued from vol. lxxiii., p. 310).

ALUMINIUM.

A large number of papers dealing with the estimation of aluminium in phosphatic materials, in which the iron is separated with NaHO, or the Al estimated by difference after determining the Fe volumetrically, are mostly unnoticed, because such processes are in principle very well known, and in steel works practice have only a limited application.

I. Separation from other Elements.

Iron.—

1406. Reynolds (*C. N.*, ii., 208).—Add oxalic acid to keep up Al_2O_3, pour into AmHO + Am_2S, oxidise the filtrate, and precipitate the Al with Am_2CO_3. Pisani (*C. N.*, iii., 257).—Oxalate keeps up the Al_2O_3 only for a time; heat readily causes it to separate.

1407. Dyer (*C. N.*, liii., 51).—The ammoniacal citrate solution of the oxides is treated with Am_2S, and the ferrous sulphide filtered off.

1408. Carnot (*C. N.*, xliv., 85).—Add tartaric acid, and precipitate Fe with Am_2S; Al is precipitated from the acetic filtrate as $AlPO_4$. In order to separate Al from Cr, the latter must be oxidised to CrO_3.

1409. Deville (*C. N.*, v., 102).—Heat $Al_2O_3 + Fe_2O_3$ in H + HCl, and weigh the residual alumina. A similar process is used by L'Hôte (*C. N.*, lv., 176), Koninck (*C. N.*, lxix., 13), and Rozycki (*J. I. S. I.*, 1893, ii., 414).

1410. Gooch and Havens (*C. N.*, lxxx., 39).—Fe is volatilised and separated from Al in HCl containing Cl at lower temperatures than with HCl alone.

1411. Wöhler (*C. N.*, xviii., 154).—Boil neutralised solution with thiosulphate to expulsion of SO_2. Al_2O_3 is precipitated.

1412. Parnell (*C. N.*, xxi., 54).—To slightly acid solution add "hypo." more than equivalent to free acid, and boil only ten or fifteen minutes.

1413. Flight (*C. N.*, xxxi., 214).—Boil faintly acid solution (containing P_2O_5) for several hours with excess of hypo.

1414. Donath and Jeller (*J. S. C. I.*, 1887, 458).—After boiling with hypo., the filtrate should be boiled down one-half to recover small amounts of Al_2O_3. The precipitate must be strongly ignited in order to get rid of the sulphur.

1415. Esilmann (*C. N.*, xxviii., 209).—To warm dilute solution, containing free acid and excess P_2O_5, add hypo. and acetic acid; boil twenty minutes, and collect $AlPO_4$.

1416. Warington (*C. N.*, x., 1).—Precipitate the acid solution (of mineral phosphate) with NaHO; digest, and estimate Al in filtrate. Also Jones (*C. N.*, liii., 87), Gladding (*C. N.*, lxxiv., 146), and many others.

1417. Lasne (*C. N.*, lxxiv., 309).—As 1416. $AlPO_4$ is soluble in acetic solutions. True $AlPO_4$ is formed by boiling with hypo. only when a certain excess of P_2O_5 is present.

1418. Glaser (*J. C. S.*, lxiv., ii., 346).—The mixed phosphates are fused with Na_2CO_3; Al can then be completely boiled out with water.

1419. Lyte (*C. N.*, xxviii., 324) and Beckman (*C. N.*, xliv., 226).—A boiling solution of $Ba(HO)_2$ separates Fe and Al perfectly, and so dispenses with the preparation of pure soda, &c.

1420. Glaser (*J. S. C. I.*, 1897, 936).—To nearly neutral and cold solution add Na_2O_2 until the solution becomes quite clear. Boil to decompose soda ferrate, and filter off $Fe_2(HO)_6$.

1421. Thomson (*C. N.*, liv., 252).—Add AmĀ to neutral FeO solution containing P_2O_5. Separate a little Fe from precipitate with NaHO, and estimate as $AlPO_4$. If Mn is present, the first separation is made, omitting P_2O_5. Neither the "NaHO" nor hypo. separation of Al from large amounts of iron is satisfactory.

1422. Parry and Morgan (*C. N.*, lxvii., 308).—Mainly as 1421; omitting the P_2O_5, and precipitating finally as Al_2O_3.

1423. Donath (*C. N.*, xlvi., 12).—Reduce with hypo., pour into alkaline KCN, acidify with HCl, and precipitate Al with Am_2CO_3. Regelsberger (*J. S. C. I.*, 1891, 1033) precipitates the Al finally by boiling with $AmNO_3$.

1424. Moore (*C. N.*, lvii., 125).—Add excess $NaHCO_2$ to FeO solution, and then form ferrocyanide by adding to KCN. Boil with AmCl to precipitate Al. Separates also Ni and Co from Al.

1425. Borntträger (*C. N.*, lxvii., 204).—Precipitate oxides together from neutral solution with potassium oleate, and dissolve out the iron oleate with hot petroleum.

1426. Vignon (*C. N.*, li., 165).—Mix the solution with large excess of trimethylamine, and allow to stand twenty-four hours; the precipitated Al is completely re-dissolved.

1427. Hess and Campbell (*C. N.*, lxxxi., 158).—From neutral and reduced solution precipitate Al (together with all the P_2O_5) with phenylhydrazine. Cr is also precipitated; but neither Fe, Ca, Mg, Mn, Co, or Ni are.

1428. De Koninck (*C. N.*, lxii., 19).—Add nitroso-β-naphthol to acetic acid solution; the Fe only is precipitated. See 25 and 26 for other separations with this reagent.

1429. Gooch and Havens (*C. N.*, lxxiv., 296).—Al_2Cl_6 is is almost insoluble in etherised HCl; Fe_2Cl_6 easily soluble. Precipitated Al_2Cl_6 ignited under HgO to Al_2O_3.

1430. Beilstein and Luther (*C. N.*, lxvi., 37).—Evaporate HNO_3 solution on water-bath, and dissolve out basic aluminium nitrate with water.

1431. Marchal and Wiernik (*J. C. S.*, lxiv., ii., 49).—Neutralise acid solution and boil with freshly precipitated MnO_2. The filtrate contains Al (and Cr); the Fe remains with the undissolved MnO_2.

1432. Kohn and Woodgate (*J. S. C. I.*, 1889, 260).—Electrolytic separation from oxalate solutions. Engels (*J. S. C. I.*, 1898, 796).—From solution containing Rochelle salt.

Manganese.—

1433. Gibbs (*C. N.*, xi., 102).—By boiling neutral solutions with soda acetate, Al is precipitated free from Mn, Ni, Co, Zn, Mg, Ca, and Ur. A second precipitation is more necessary than in the like Fe separation.

1434. Leffler (*C. N.*, lxxvii., 265).—$Al_2Cl_6.11{\cdot}5Al_2(HO)_6$ may be formed by neutralising Al_2Cl_6 solutions with dilute alkalis. The acetate precipitation separates Mn, but not Ni, quantitatively. The separation of Ni by Na_3PO_4 in acetic solutions is approximately accurate.

1435. *Chromium.*—Brearley (*C. N.*, lxxvii., 179).—Al is not separated from CrO_3 by precipitating with AmHO, Am_2CO_3, or acetates, and a considerable excess of Na_2CO_3 is needed. It may be separated by Na_3PO_4 in acetic solutions.

Magnesia and Lime.—

1436. Wrinkle (*C. N.*, xxii., 4).—The amount of MgO

which goes down on precipitating Al with AmHO depends on the presence of SO_3 and the mode of adding AmHO.

1437. ROSE (*C. N.*, ii., 291).—By adding AmHO and boiling off excess, any Ca precipitated by CO_2 impurities is re-dissolved if ammonium salts are present.

Copper, Zinc, Mercury, &c.—

1438. HAVENS (*C. N.*, lxxviii., 53).—Cu, Zn, Hg, and Bi are separated as in 1429.

1439. JANNASCH (*J. C. S.*, lxxvi., ii., 60).—Hg is precipitated by ammoniacal hydroxylamine in the presence of oxalic acid.

1440. *Zircon.*—DAVIS (*C. N.*, lix., 100).—Zr is precipitated from nearly neutral solutions with soda iodate. Al remains in solution.

Beryllium.—

1441. ZIMMERMAN (*C. N.*, lviii., 49).—Boil with KHO; Be is precipitated. Or boil neutral solution with hypo.; Al is precipitated.

1442. HAVENS (*C. N.*, lxxvi., 111).—As in 1429.

II. Gravimetric Estimations.

1443. PENFIELD and HARPER (*C. N.*, liv., 91).—Some instructive experiments on the precipitation and washing of $Al_2(HO)_6$.

1444. GUYARD (*C. N.*, xlviii., 119).—Alumina precipitated in the presence of glycerin falls in dense flocks which are easily washed.

1445. LUCKOW (*C. N.*, xi., 205).—Precipitate with bicarbonates rather than carbonates, as the precipitate is less bulky and more easily washed. The smaller excess of AmHO and larger of Am_2S used for precipitating the better. Cochineal colours Al solutions carmine.

1446. ALLEN and GOTTSCHALK (*J. S. C. I.*, 1900, 1149).—The Al is precipitated as basic carbonate by passing CO_2 into a solution which contains only a small excess of KHO.

1447. MOISSAN (*C. N.*, lxxiii., 49).—Am_2S (with reasons), and not AmHO, is used for precipitating Al. Al_2O_3 is difficult to dehydrate. Estimates also Si, Fe, C, Cu, and Na in Al alloys.

1448. LUNGE (*J. S. C. I.*, 1890, 111).—On precipitating Al with AmHO, the excess need not be boiled off if AmCl is present; the precipitate retains no SO_3.

1449. STEAD (*J. S. C. I.*, 1889, 966).—Dissolve Fe in HCl, separate SiO_2, and boil nearly neutral solution with Na_3PO_4 and $Na_2S_2O_3$. Dissolve precipitated $AlPO_4$ in HCl, separate little Fe with NaHO and re-precipitate Al as before. PHILLIPS (*C. N.*, lxi., 313) describes a similar process, and so does CARNOT (*C. N.*, lxiii., 10 and 172), except that the $AlPO_4$ first obtained is purified by re-precipitating in the same way.

1450. OSMOND (*J. I. S. I.*, 1890, ii., 200).—Heat steel in current of HCl; the Al in the residue is estimated by difference after deducting S and P.

1451. DROWN and M'KENNA (*C. N.*, lxiv., 194).—The steel solution, freed from C and SiO_2, is electrolysed, using Hg cathode. The Fe forms an amalgam, and the Al is precipitated from filtered solution as $AlPO_4$.

1452. SCHŒNISS (*J. I. S. I.*, 1892, ii., 518).—Evaporate HNO_3 solution, fuse evaporated residue with NaHO in silver dish, and precipitate Al from acidulated filtrate with AmHO.

1453. ZIEGLER (*C. N.*, lxvi., 321).—Fuse powder (with or without oxidation by acids), and precipitate as $Al_2(HO)_6$ after filtering off the iron.

1454. ZIEGLER (*J. I. S. I.*, 1891, i., 440).—Dissolve Fe in HCl, complete reduction to FeO with hypophosphite, and add excess ZnO. Dissolve precipitate in HCl, and eliminate impurities by precipitating with AmHO both before and after fusing with soda carbonate.

1455. LEDEBUR (*J. I. S. I.*, 1893, ii., 534).—Treat strong HCl solution of Fe_2Cl_6 with ether (see 1429). Precipitate Al in aqueous solution as $AlPO_4$ with Na_3PO_4 and acetate.

1456. KLEMP (*C. N.*, lxii., 241).—Treat Al metal with KHO, burn liberated H to H_2O, and calculate per cent Al from increased weight of H_2SO_4 tube.

1457. REGELSBERGER (*J. C. S.*, lxii., 102 and 535).—Dissolve Al metal in KHO, boil with $AmNO_3$, and collect precipitated Al_2O_3. KHO completely dissolves Al from its Ni or Cu alloy.

1458. REGELSBERGER (*J. C. S.*, lxiv., ii., 48).—Estimate Al in Fe-Al alloy by process 1423; and gives means of analysing Al-Cu and Al-Zn alloys. JUPTNER (*J. C. S.*, lxiv., ii., 391) calls 1423 Neuhausen's method.

1459. THOMSON (*J. S. C. I.*, 1886, 152).—Precipitate Al and Fe together as phosphates, and determine Fe volumetrically and Al by difference. $AlPO_4$ becomes basic on washing with H_2O.

1460. MACIVOR (*C. N.*, xxix., 199).—The ignited $Al_2O_3+Fe_2O_3$ are dissolved in H_2SO_4 in the presence of zinc prior to the Fe titration.

1461. GLASER (*J. C. S.*, lxii., 1523).—Precipitation of Al solution containing excess P_2O_5 with AmHO or $Am\overline{A}$ at 100° gives basic phosphates; at 70°, $AlPO_4$ exactly is formed

1462. HUNT, CLAPP, and HANDY (*C. N.*, lxv., 223 and 235).—Analysis of Al metal. Al estimated as $AlPO_4$ by boiling with hypo.

1463. HANDY (*C. N.*, lxxv., 55, 66, 79).—Estimation of Cu, Fe, Si (total and graphitic), Na, and C in Al. Al_2O_3 is very hygroscopic. Analysis of the Cu, Ni, Mn, Cr, W, Ti, and Zn alloys of Al, Al solders, and the raw materials of Al manufacture.

1464. CAMP (*C. N.*, lxxxii., 91).—In ore and cinders the HCl filtrate from SiO_2 is neutralised and $AlPO_4$ precipitated by boiling with $Am\overline{A}$ and hypo. $AlPO_4$ is slightly soluble in the wash-water.

III. Volumetric Estimations.

1465. REISS (*C. N.*, xlvii., 248).—To boiling acetic solution containing $CaCl_2$ add standard $Am\overline{O}$ until a turbidity appears; 3 $Am\overline{O}$ = 1 Al_2O_3.

1466. PRUNIER (*C. N.*, l., 235).—The neutral solution of Al, using tropæoline indicator, is precipitated by N/2 AmHO, and the excess determined in a fraction of the filtrate.

1467. NEUMANN (*J. C. S.*, lxviii., ii., 64).—Precipitate with standard alkaline sulphide, add H_2SO_4 to portion of filtrate, and titrate with KHO.

1468. LESCŒUR (*J. C. S.*, lxxiv., ii., 484).—Make solution neutral to helianthin, add excess of alkali, boil, and titrate back with acid, using phenolphthalein.

1469. BAYER (*C. N.*, lii., 277).—Add NaHO in excess, and titrate with litmus as indicator in one portion and tropæoline in another. ATKINSON (*C. N.*, liii., 311) uses phenolphthalein instead of litmus. See also BAYER (*C. N.*, liii., 40), LUNGE (*J. S. C. I.*, 1890, 767), CROSS and BEVAN (*J. S. C. I.*, 1890, 202; and 1891, 314), and E. B. (*J. C. S.*, l., 651).

1470. KRETZSCHMAR (*J. S. C. I.*, 1890, 1064).—Add standard Na_3PO_4 and $Am\overline{A}$, and determine excess of P_2O_5 with uranium acetate. Any Fe present is estimated with $KMnO_4$, and its $FePO_4$ equivalent deducted.

1471. STOCK (*J. S. C. I.*, 1900, 277).—On adding KI and KIO_3 to Al solutions, $Al_2(HO)_6$ is precipitated and I liberated. The I is estimated with hypo. at boiling-point.

(END OF PART X.).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING OCTOBER 31ST, 1901.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, November 9th, 1901.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 216 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Oct. 1st to Oct. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 216 samples examined by us during the month, all were found to be clear, bright, and well filtered.

We have to record a further serious deficiency in the rainfall at Oxford during the month of October. The actual amount of rain measured was 1·18 inches, fairly well distributed throughout the month; the average fall for the month is 2·76 inches; this leaves a deficit of 1·58 inches, and, added to the previous deficit, 0·92 inch, makes a total deficitof 2·50 inches, or 12 per cent on the thirty-five years' average.

Our bacteriological examinations of 563 samples have given the results recorded in the following table; we have also examined 56 other samples, from special standpipes, wells, &c., making a total of 619 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 27 samples) ..	173
New River, filtered (mean of 136 samples) ..	4
Thames, unfiltered (mean of 27 samples) ..	865
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 307 samples)	13
Ditto ditto .. .. highest	315
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 27 samples) ..	155
River Lea, from the East London Company's clear-water wells (mean of 39 samples) ..	12

Of the 482 samples of impounded and filtered water supplied to London and examined bacteriologically during the past month, 28 samples, or 5·8 per cent, were sterile. Only one sample contained more than 150 microbes, while only seven samples, or 1·4 per cent, contained more than 100 microbes per c.c. The mean number of microbes in the seven excess samples was 149, against a corresponding mean of 118 in eight excess samples during September.

The remarkable purity of the London water at this time of year is no doubt partly due to the very small rainfall in the valleys of the Thames and Lea.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

THE QUANTITATIVE SEPARATION AND DETERMINATION OF URANIUM.*

By EDWARD F. KERN.

(Continued from p. 239).

PART II.—THE DETERMINATION OF URANIUM.

Determination of Uranium as Oxide.

THE precipitant which Péligot used in 1840 for the estimation of uranium was ammonia, the principal reagent used for that purpose at the present time. The yellow precipitate which forms when ammonia is added to a uranyl solution is hydrated ammonium uranate (*Chemiker Kalendar*, 1899, p. 270), $(NH_4)_2U_2O_7.xH_2O$, or $(NH_4)_2O.2UO_3.xH_2O$, which is soluble in alkali carbonate solutions, and slightly soluble in pure water; but in water containing ammonia, ammonium nitrate, or ammonium chloride it is insoluble (Comey's "Dictionary of Chemical Solubilities"). The presence of tartaric acid, oxalic acid, or non-volatile organic substances prevents the precipitation of ammonium uranate (Fresenius's "Qualitative Chemical Analysis," 219).

If the solution contains any alkalis or alkaline earths, a portion of these will be precipitated along with the uranium (Fresenius's "Qualitative Chemical Analysis," Sixth Edition, p. 533).

Berthier's Method (*Liebig's Ann. Chim.*, xlvi., 184).—The reagent next in importance to ammonia, for the estimation of uranium, is ammonium sulphide, which was first used (in 1840) by Berthier. A complete precipitation of uranium by ammonium sulphide is obtained, provided the solution is previously nearly neutralised by ammonia, and no carbonates are present. The precipitate which forms is usually black in colour, sometimes changing to reddish-brown (*Pogg. Ann.*, cxvi., 352). When a large excess of the precipitant is added, and it is allowed to stand, the liquid sometimes assumes a brown colour (*Pogg. Ann.*, cxxiv., 120). This colour, says Zimmerman (*Liebig's Ann. Chim.*, 1880, cciv., 224), is due to the solubility of uranyl sulphide in ammonium carbonate contained in the ammonium sulphide. When the ammonium sulphide contains a considerable amount of thiosulphate the red sulphide described by Remele (*Pogg. Ann.*, cxvi., 352) is formed; but when thiosulphate is absent only the dark precipitate results. Thiosulphate in the reagent is due to the oxidation of ammonium sulphide by atmospheric oxygen.

In 1865, A. Remele studied the method for the estimation of uranium by the use of ammonium sulphide, and found the best results were obtained by the following procedure (*Zeit. Anal. Chem.*, iv., 379);—The ammonium sulphide should be fresh, and kept well corked, as it absorbs carbon dioxide when exposed to the atmosphere. To the nearly neutral ammoniacal solution, add an excess of yellow ammonium sulphide, and keep the solution near boiling for an hour, in order to convert the $(UO_2)S$, which is first formed, into a mixture of UO_2 and sulphur. This precipitate is rapidly dissolved by alkali carbonates and by tartaric acid. It is slightly soluble in pure water, is soluble in dilute, but insoluble in absolute, alcohol. It is readily soluble in acids, even acetic acid (Comey's "Dictionary of Chemical Solubilities," 1896). The presence of ammonium chloride or ammonium nitrate assists the precipitation of $(UO_2)S$, as it is less soluble in these solutions. The precipitate, containing all the uranium, is filtered off, and washed with cold or hot water containing a small amount of ammonium sulphide and ammonium chloride or nitrate. Wash first by decantation, and finally on the filter. The precipitate during washing passes to yellow uranic hydroxide. It is dried, then roasted to remove all the sulphur, and finally converted

* Contribution from the Havemeyer Laboratories of Columbia University. From the *Journal of the American Chemical Society*, xxiii., No. 10.

TABLE IV.

(The theoretical amount of uranium taken was 0·1925 grm.).

Expt. No.	Approximate dilution.	Salts present.	Crucible in which ignited.	Weighed as—	Weight of U_3O_8.	Uranium equivalent of U_3O_8.	Ignited in hydrogen for— Hours.	Weight of UO_2.	Uranium equivalent of UO_2
	c.c.								
1.	200	NH_4Cl	Platinum	U_3O_8	0·2242	0·19130	—	—	—
2.	200	NH_4Cl	Platinum	U_3O_8	0·2268	0·19252	—	—	—
3.	150	NH_4Cl	Platinum	U_3O_8	0·2269	0·19260	—	—	—
4.	150	NH_4Cl	Platinum	U_3O_8	0·2266	0·19235	—	—	—
5.	175	NH_4Cl	Platinum	U_3O_8	0·2268	0·19252	2	0·2191	0·19329
6.	175	NH_4Cl + $CHCl_3$	Platinum	U_3O_8 + UO_2	0·2267	0·19243	¾	0·2179	0·19223
7.	175	NH_4Cl + $CHCl_3$	Porcelain	U_3O_8	0·2269	0·19260	2½	0·2207	0·19479
8.	150	NH_4Cl	Platinum	U_3O_8	0·2268	0·19252	1	0·2211	0·19505
9.	150	NH_4Cl	Platinum	U_3O_8	0·2270	0·19268	¾	0·2221	0·19593
10.	150	NH_4Cl + Alcohol	Porcelain	U_3O_8	0·2280	0·19353	—	—	—
11.	175	NH_4Cl + Alcohol	Porcelain	U_3O_8	0·2270	0·19268	—	—	—
12.	175	NH_4Cl	Platinum	UO_2	—	—	½	0·2180	0·19232
13.	150	NH_4Cl	Porcelain	—	—	—	1	0·2240	0·19761

TABLE V.—*Precipitation of Uranium by Disodium Hydrogen Phosphate.*

Expt. No.	Approximate dilution.	Salts added.	Temperature of solution after precipitation.	Crucible in which ignited.	Time of ignition.	Weight of $(UO_2)_2P_2O_7$.	Uranium equivalent.	Theoretical amount of uranium taken.
	c.c.				Minutes.			
1.	150	NH_4NO_3 + $NH_4C_2H_3O_2$	Cold, then heated to boiling-point	Platinum	15	0·2875	0·1921	0·1925
2.	150	NH_4Cl + $NH_4C_2H_3O_2$	,, ,,	,,	10	0·2884	0·1927	0·1925
3.	150	NH_4NO_3 + $NH_4C_2H_3O_2$	,, ,,	Porcelain	10	0·2878	0·1923	0·1925
4.	150	NH_4NO_3 + $NH_4C_2H_3O_2$	Boiling-point for one hour after precipitation	Platinum	10	0·2851	0·1905	0·1925
5.	150	Chloroform + $NH_4C_2H_3O_2$	,, ,,	,,	10	0·2848	0·1903	0·1925
6.	150	NH_4NO_3 + $NH_4C_2H_3O_2$	,, ,,	Porcelain	15	0·2875	0·1921	0·1925
7.	150	Chloroform + $NH_4C_2H_3O_2$	,, ,,	,,	20	0·2870	0·1918	0·1925

into U_3O_8 by ignition in the air, or into UO_2 by ignition in a current of hydrogen, and allowing to cool in same.

A complete separation of uranium from the alkalis and alkaline earths is obtained by means of ammonium sulphide (*Zeit. Ann. Chem.*, i., 411).

C. Winkler made a comparison of this method with Péligot's ammonium method (Fresenius's "Quantitative Chemical Analysis," p. 281), and states that the precipitation of uranium by pure ammonium sulphide is trustworthy (CHEM. NEWS, 1881, xliii., 153).

Experimental.

Precipitation of Uranium by Ammonia.—For each determination a measured amount of standard uranium nitrate solution was run into a beaker, and enough distilled water added to bring the volume to from 150 to 200 c.c. The solutions were brought to boiling, and a few drops of nitric acid added, and the uranium precipitated by adding an excess of ammonia to the hot solution. The precipitates which formed were a bright lemon-yellow colour, and settled rapidly. The precipitates were allowed to settle, and washed several times by decantation, and twice on the filter with warm dilute ammonium chloride solution (2 grms. salt to 100 c.c. water), after which they were dried in a hot oven, and ignited and weighed as oxides.

Table IV. gives the conditions observed.

U_3O_8 multiplied by 0·84884 gives the uranium equivalent; UO_2 multiplied by 0·88218 gives the same. These are the factors obtained by taking the atomic weight of uranium as 239·6, and that of oxygen as 16 (*Journ. Amer. Chem. Soc.*, 1901, xxiii., 94).

For all the above precipitations the solutions, of from 150 to 200 c.c. volume, were made decidedly acid with from 0·5 to 1 c.c. nitric acid (sp. gr. 1·42), brought to boiling, and ammonia added in excess. Some of the solutions were boiled for about fifteen minutes after the precipitation by ammonia, while others were filtered directly without boiling. The boiling caused the lemon-yellow coloured voluminous amorphous precipitate to change to a more crystalline form, less voluminous, and of a slightly darker colour. The precipitates which were boiled were much easier to filter and wash, and were less liable to pass through, which usually happened when boiling was omitted.

The presence of chloroform or alcohol (as recommended by some chemists) did not assist the precipitation, but the presence of ammonium chloride or ammonium nitrate was essential. Five to ten grms. were added previous to the addition of ammonia.

Some of the precipitates were ignited separate from the paper, and others without separating from the paper. The results obtained, whether the precipitates were ignited separately or not, were identical, showing that it is unnecessary to ignite the precipitate and the filter paper separately, as is recommended by the German chemists.

When the uranium was weighed as U_3O_8, the precipitates together with the filter paper were placed in a crucible and slowly ignited till the paper had completely burned; then the ignition was continued for about fif-

teen minutes in a blast-flame, and allowed to cool slowly in a gradually decreasing Bunsen flame. During ignition the crucibles were placed in a slanting position in order to allow of free circulation of air in the crucible, thus obviating complete oxidation. The results were the same whether porcelain or platinum crucibles were used.

In all directions given in text-books and journals for weighing uranium as oxide, it is recommended that the dry precipitate of ammonium uranate be strongly ignited over a blast lamp to U_3O_8, and allowed to slowly cool in a gradually decreasing flame and finally in a desiccator. It is then weighed, and as a means of ascertaining its purity for the purpose of control, it is re-ignited in a current of pure hydrogen and reduced to its lower oxide, UO_2. This was tried, but only in one case was it possible to completely reduce U_3O_8 to UO_2, even when the ignition in hydrogen was continued for two hours. This time (experiment No. 6) the reduction was brought about by using a platinum crucible, and igniting strongly in a current of pure hydrogen over the hottest blast-lamp that could be obtained. When a porcelain crucible was used in which the ignition was made, the reduction did not proceed so far as when a platinum crucible was used. The reason for this is the fact stated by Roberts-Austen ("Introduction to Metallurgy," 1898, p. 54) as follows:—"Sainte Claire Deville and Troost discovered that hydrogen and hydrocarbons pass through platinum at a red heat." The further reduction of U_3O_8, when a platinum crucible is used, would seem to indicate that hydrocarbons of the flame play as important a part in the reduction as the hydrogen. It was impossible to obtain a single complete reduction of the precipitate to UO_2 when a porcelain crucible was used, even when the precipitate was not previously ignited. When a platinum crucible was used, and the precipitate not previously ignited in the air, the complete reduction to UO_2 occurred within half-an-hour by igniting it in a current of pure hydrogen over a blast-lamp, and allowing it to cool in an atmosphere of hydrogen over a gradually decreasing flame. The U_3O_8 is a velvety black coloured mass, and the UO_2 a dull brown coloured mass.

For the above reductions ordinary porcelain and platinum Rose crucibles were used. The hydrogen was purified by Schobig's method (*Journ. Prakt. Chem.*, [2], xiv., 289—299), by first passing it through a strong solution of potassium permanganate to remove the hydrides of arsenic, antimony, phosphorus, and carbon; then through a strong solution of caustic soda to remove hydrogen sulphide; and finally through sulphuric acid (sp. gr. 1·84) to remove moisture.

Determination of Uranium as Phosphate.

Review of Method.

The precipitation of uranium by an alkali phosphate has rarely been employed as a means of estimating uranium, because the precipitate which forms is gelatinous and difficult to wash free from alkali. This trouble has been overcome by adapting the method to volumetric means, which is the reverse of the volumetric estimation of phosphoric acid by a standard uranium solution. The uranium in solution as acetate is titrated by means of a standard solution of sodium-hydrogen-ammonium phosphate ($NaHNH_4PO_4$), which is added till a drop of the precipitated solution brought in contact with a drop of freshly prepared solution of potassium ferrocyanide does not give a brown colouration (Mohr's "Lehrbuch der Chemisch-analytischen Titrirmethode," p. 521; Dammer's "Handbuch der Anorg. Chemie," 1893, iii., 686).

The quantitative estimation of uranium by means of an alkali phosphate was first suggested by Leconte (Liebig and Kopp, *Jahresbericht*, 1853, p. 642), and later worked out by Pisani (Chem. News, 1862, iii., 211); but owing to the difficulty of filtering and washing the greenish-yellow, slimy precipitate of UO_2HPO_4, this method has not come into use.

Experimental.

Were it not for the difficulty of washing the uranium phosphate, which is formed by disodium hydrogen phosphate, this method would afford a decided advantage over precipitating it with ammonia, and weighing it as oxide (U_3O_8), because any error would be greatly diminished by weighing as $(UO_2)_2P_2O_7$. U_3O_8 multiplied by 0·84884 gives the uranium equivalent, while $(UO_2)_2P_2O_7$ multiplied by 0·66815 gives the same; so by weighing the uranium as pyrophosphate the error or loss is decreased.

This method was studied, and the best conditions for weighing uranium as uranyl pyrophosphate were worked out, the results of which are tabulated (see Table V.).

These determinations were made by measuring 50 c.c. of standard uranium nitrate solution into a beaker, diluting to 150 c.c., and adding nitric acid (sp. gr. 1·42), varying the amount from 0·5 c.c. to 1·5 c.c. The solutions were brought to boiling, and ammonia (sp. gr. 0·90) added to neutral reaction and a measured amount in excess—from 1 c.c. to 10 c.c. The yellow precipitate of ammonium uranate was dissolved by adding 50 per cent acetic acid till the precipitate disappeared, and then an excess varying from 1 c.c. to 5 c.c. To the solution—which contained besides uranium acetate, an excess of acetic acid, ammonium nitrate, and ammonium acetate—an excess of a saturated solution of disodium hydrogen phosphate was added. The precipitate which formed was greenish white in colour, and voluminous. The solution was brought to boiling, then allowed to cool, and filtered. In experiments Nos. 4 to 7 the solutions were kept for one hour on water-baths at the temperature of boiling water, after which they were allowed to cool, then filtered. This treatment assisted the settling of the precipitate, but did not change its gelatinous character.

The washing of the precipitates was done by four decantations, and twice on the filter with a hot dilute solution of ammonium chloride (2·5 grms. of salt to 100 c.c. of water). The washing was not so easy as the ammonium uranate precipitates, even when as much as 5 grms. of ammonium chloride were added to the solution previous to its precipitation. Neither the addition of chloroform nor of ammonium chloride had any effect on the appearance of the precipitate, as there were already sufficient ammonium salts present, formed by the neutralisation of nitric acid by ammonia, and of ammonia by acetic acid.

The precipitates, after washing, were dried at a temperature of from 100° C. to 115° C., separated from the filter-paper, which was first ignited in the crucible, then the precipitate added, and the ignition continued for from ten to twenty minutes at "redness" over a Bunsen burner. The residue in most cases was green in colour, due to the partial reduction of uranyl pyrophosphate. Whenever the temperature of ignition was above "redness" a reduction always occurred, especially when a platinum crucible was used. When a porcelain crucible was used the ignition could be done at "redness," but above this temperature (as over a blast-lamp) reduction always resulted.

The reduced uranyl pyrophosphate was not weighed as such, but was moistened with a few drops of nitric acid (sp. gr. 1·42), dried over a low flame, and re-ignited at "low redness," over a Bunsen burner. The mass after such treatment was always of a lemon-yellow colour. The weight of the yellow uranyl pyrophosphate remained constant, no matter how long it was ignited at a temperature not exceeding "low redness," but above this temperature it always lost weight, and assumed a green colour. Whenever this occurs it may be re-oxidised by treating it with nitric acid, and re-igniting at "low redness."

This green residue of pyrophosphate most probably has the composition $U_2O_3.P_2O_7$, which is indicated by the weights of several which varied from 0·2820 to 0·2827 grms. 0·2820 multiplied by 0·6853 gives 0·1929 grm. uranium, the theoretical amount of uranium being 0·1925 grm.

One of the residues which was more intensely ignited than the others, with the cover on the platinum crucible, was of a reddish-brown colour. Its weight was 0·2800 grm., showing that the reduction had gone further than $U_2O_3.P_2O_7$.

The composition of the lemon-yellow coloured uranyl pyrophosphate is $(UO_2)_2P_2O_7$.

(To be continued).

THE ACTION OF SODIUM THIOSULPHATE ON SOLUTIONS OF METALLIC SALTS AT HIGH TEMPERATURES AND PRESSURES.*

By JOHN T. NORTON, Jun.

THE use of sodium thiosulphate as a substitute for hydrogen sulphide in effecting precipitations, and its application in the case of arsenic, antimony, copper, and platinum, was suggested by Himly (*Liebig's Ann. Chem.*, lxiii., 150) before the middle of the last century. Thirteen years later Vohl (*Liebig's Ann. Chem.*, xcvi., 237), and Slater (*Chemical Gazette*, 1855, p. 369), independently, drew attention to this use of sodium thiosulphate, and extended the investigation to salts of tin, mercury, silver, gold, lead, bismuth, and cadmium. Slater, in addition, studied the action of sodium thiosulphate upon chromic acid, molybdates, ferrous and ferric ferrocyanides, ferric sulphocyanide, and potassium permanganate. Following out these lines, the precipitation of copper, together with arsenic and antimony, by treating with sodium thiosulphate the hot solution containing sulphuric acid, and the separation of these elements from tin, zinc, iron, nickel, cobalt, and manganese, has been advocated by Westmoreland (*Journ. Soc. Chem. Ind.*, v., 51); and quite recently Faktor (*Centralblatt*, 1900, ii., 20, 67, 239, 594) has studied the action of sodium thiosulphate upon neutral salts of several of the elements mentioned, as well as the modifying influence of ammonium chloride and other salts upon the course of the reaction.

Subsequently to the work of Himly, Vohl, and Slater, Chancel (*Comptes Rendus*, xlvi., 987) developed his well-known method for the precipitation of aluminum as the hydroxide and its separation from salts of iron, by boiling with sodium thiosulphate, the nearly neutral solution, containing the salts of aluminum and iron, at suitable dilution; and upon an extension of the principle of Chancel's separation of aluminum from iron, Stromeyer (*Liebig's Ann. Chem.*, cxiii., 127) founded his well-known processes for the separation of titanium and zirconium from iron. The latter process appears to be fairly trustworthy; but of Chancel's method, although it has met with wide acceptance, it was shown by Wolcott Gibbs very soon after its announcement (*Zeit. Anal. Chem.*, iii., 389) that it fails to bring about complete separation of alumina within a reasonable period of boiling, and this result has been confirmed by Zimmerman ("Inaug. Diss.," Berlin, 1887), who has shown that the boiling must be continued fifteen hours in order to complete the precipitation of the alumina.

It was shown by Dr. Gibbs that when the treatment of salts of aluminum by thiosulphate was carried on in sealed tubes under pressure at 120° C., the precipitation of alumina was complete, and further that the precipitation of sulphides of nickel, cobalt, and iron, though partial under ordinary atmospheric pressure, was made complete by heating in sealed tubes to 120—140° C.

In repeating the experiments of Dr. Gibbs qualitatively and extending them, I have made use of the well-known Pfungst tube to secure the necessary pressure. In each experiment a test-tube containing the mixture of an excess of sodium thiosulphate with the salt whose action was studied was placed within the Pfungst tube containing some water; the cover of the latter was set in place, and firmly bolted upon a washer of lead, and the whole was submitted to temperatures varying from 140° to 200° C. for an hour by immersing in a bath of paraffin. After cooling, the test-tube was taken out, the precipitate was filtered off, and the filtrate tested by appropriate reagents to determine the completeness of precipitation. The following table records the details of these experiments:—

TABLE I.—*Action of $Na_2S_2O_3$ on Salts under Pressure.*

Salts used.	Precipitates.	Degree of precipitation.
	Sulphides.	
$NiSO_4$	$NiS+S$	Complete.
$CoSO_4$	$CoS+S$	,,
$FeCl_3$	$FeS+S$	,,
$ZnSO_4$	$ZnS+S$	,,
$PbO_2(C_2H_3O)_2$	$PbS+S$	,,
$Hg(NO_3)_2$	$HgS+S$	,,
$AgNO_3$	Ag_2S+S	,,
$CuSO_4$	$CuS,(Cu_2S),+S$	,,
$CdSO_4$	$CdS+S$	,,
$KSbC_4H_2O_7$	Sb_2S_3+S	,,
$Bi(NO_3)_3$	Bi_2S_3+S	,,
	Hydroxides.	
$NH_4Al(SO_4)_212H_2O$	AlO_3H_3+S	,,
$K_2Cr_2O_7$	CrO_3H_3+S	,,
K_2ZrF6	ZrO_4H_4+S	,,
K_2TiF6	TiO_4H_4+S	,,
$Th(NO_3)_4$	ThO_4H_4+S	,,
	Elements.	
SeO_2	$Se+S$	,,
TeO_2	$Te+S$	,,
	Sulphides.	
$MnSO_4$	$MnS+S$	Partial.
$AuCl_3$	Au_2S+S	,,
$(NH_4)_2MoO_4$	$MoS_3(?)+S$, red liquid	,,
	Hydroxides.	
$BeCl_2$	BeO_2H_2	,,
	Undetermined.	
$(NH_4)_2U_2O_7$	Black	,,
K_2PtCl_6	Grey reddish brown liquid	,,
$CeCl_3$	White-yellow liquid	,,
$CaCl_2$	,, ,,	,,
$SrCl_2$	,, ,,	,,
$BaCl_2$	,, ,,	,,
$MgSO_4$	—	Trace.
NH_4VO_3	Brown liquid	,,
H_2KAsO_4	—	,,

A perusal of this table brings to light several interesting facts. It appears that salts of nickel, cobalt, iron, zinc, lead, mercury, silver, copper, cadmium, antimony, and bismuth are completely precipitated as sulphides by sodium thiosulphate under the prevailing conditions of temperature and pressure. In the case of manganese precipitation is only partial, and arsenic does not seem to be precipitated from an arsenate without the addition of acid. Tin, curiously enough, is not thrown down as the sulphide from a stannous salt, but gives a dirty white precipitate of uncertain composition. Salts of aluminum, chromium, titanium, zirconium, and thorium are completely precipitated as the hydroxides; but in the case of beryllium, which one would expect to act similarly, the precipitation as the hydroxide is incomplete. Salts of selenium and tellurium are reduced, and the elements are precipitated. The precipitates obtained with barium, strontium, and calcium were white in a bright yellow liquid, but no study was made of the constitution of precipitate or liquid. In the case of magnesium there was no precipitate. Salts of

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. xii., No. 68.

molybdenum, vanadium, and uranium gave dark coloured liquids. Thallium yielded a white spongy mass which on compression was reduced to a very small bulk without disintegrating. Salts of gold and platinum gave slight dark precipitates, presumably sulphides, surrounded by dark colured liquids.

The apparatus used in these experiments and described above is easily handled, and answers sufficiently well for qualitative purposes. But, obviously, the introduction into precipitates of foreign matter caused by the action of water on the glass of the test-tube and porcelain lining of the Pfungst tube precludes the possibility of an exact quantitative study of the reactions involved. For the subsequent experiments, therefore, conducted upon the same general lines, a digester with an interior cylindrical cavity of about 12 c.m. in depth by 5 c.m. in diameter, and provided with a pressure gauge, was employed. As a container for the solutions to be tested use was made of a platinum cylinder 4 c.m. in diameter and 10 c.m. deep, provided with a loose cover. With this apparatus the following quantitative experiments, which deal with those elements which are precipitated as hydroxides, namely, aluminum, beryllium, chromium, zirconium, and titanium, were made:—

In each case a weighed quantity of the salt taken for the experiment was dissolved in 50 c.m. of water in the platinum vessel, and to this a known amount of sodium thiosulphate was added. The vessel was placed in the digester, and the latter was heated by a Bunsen burner in the customary way until the required pressure was shown on the gauge. The apparatus was then cooled, and the platinum vessel removed from the digester. The precipitate was filtered off on ashless paper, ignited, and weighed.

(To be continued).

NOTICES OF BOOKS.

The Chemical Essays of Charles William Scheele. Translated from the *Transactions of the Academy of Sciences at Stockholm*, with additions. With a Sketch of the Life of Karl Wilhelm Scheele, By John Geddes M'Intosh. Re-issued by Scott, Greenwood, and Co., 19, Ludgate Hill, London, E.C.

The first English publication of these essays was in 1786, the year Scheele died, and the preface to that early work is given in full; except for some references to Phlogiston and to the works of "Mr. Cavendish" and "Mr. Lavoisier" one can scarcely realise that it was written more than a century ago. In one direction, at all events, things have altered for the good; the then writer, Thomas Beddoes, laments "the very slow and imperfect manner in which the improvements in literature and science, that are made in several countries abroad, become generally known in England," and he recalls many names among the philosophers of Germany and Sweden in particular with whose contributions to the sum of human knowledge

> "the authors and professors of Britain, how confident soever of their own superiority, might find it no disadvantage to be better acquainted than they in general appear to be"!

Nous avons changé tout cela! In point of fact, at the present time the *Comptes Rendus* and the *Zeitschrift* are more accessible to the rank and file of English men of science than are the *Philosophical Transactions of the Royal Society*.

The author of the present edition has entered upon his task with an enthusiasm worthy of the subject, and the "Life of Karl Wilhelm Scheele" carries us vividly back to the times when the humble apothecary in the midst of his struggle for a livelihood found time to pursue truth for its own sake.

A glance at these essays shows at once that Scheele's great power rested in the author's painstaking investigation of minute details. Nothing was guessed at; experiment after experiment was "tried until the sought for truth stood out clearly before the toiler." Hampered as he was by the meagreness of chemical knowledge at the time his achievements are little short of marvellous. In his essays on manganese it is clear that he really discovered chlorine, although he called it dephlogistigated muriatic acid, for if we substitute hydrogen for phlogiston we get dehydrogenised muriatic acid; in a word, chlorine. Scheele found a true friend in Bergmann, of whom it was said "the greatest of Bergmann's discoveries was the discovery of Scheele."

The achievements of this indefatigable chemist are too numerous to recount. Among the most prominent are the discovery of glycerin, citric, malic, oxalic, and gallic acids, arsenate of copper (Scheele's green), and sulphuretted hydrogen. His work on the action of light and heat upon silver, on ether, prussian blue, milk, and sugar of milk, carry us back to the days when the chemical world was young, and we wonder to what heights he would have risen had it been his fortune to have lived a century later.

For the collection and arrangement of the essays and the sketch of the life of this remarkable man we offer the author our hearty congratulation, and would recommend the book as a refreshing recreation to the hard-worked student or investigator of the present day.

Notes on Essential Oils, with Special Reference to their Use, Composition, Chemistry, and Analysis. By T. H. W. Idris, F.C.S. With Tables of Constants of the more commonly occurring Oils. Second Edition. London: Idris and Co., Pratt Street, Camden Town,

The first edition of this practical and useful little book appeared about three years ago, and was so well received that the author has felt justified in bringing out a second edition. Much new matter and recent formulæ have been added, but the character of the work, that of a laboratory note-book, remains the same. For fuller information the reader is referred to standard text-books, particularly one that has recently appeared, by E. J. Parry, from whose work the author gives, in the form of an appendix, "a table of constants of the more important essential oils," including source, yield per cent, specific gravity, optical rotation, and constituents.

The book will undoubtedly maintain its reputation for usefulness to analysts and manufacturers. There is both a table of contents and a good index.

A Dictionary of Dyes, Mordants, and other Compounds used in Dyeing and Calico Printing. By Christopher Rawson, F.I.C., F.C.S., Consulting Chemist to the Behar Indigo Planters' Association, co-author of "A Manual of Dyeing"; Walter M. Gardner, F.C.S., Head of the Department of Chemistry and Dyeing, Bradford Municipal Technical College; and W. F. Laycock, Ph.D., F.C.S., Analytical and Consulting Chemist. London: Charles Griffin and Co., Limited, Exeter Street, Strand, W.C.

The work has been prepared as a companion to Mr. Rawson's "Manual of Dyeing," published in 1893. It comprises a general description of dyes, mordants, and other substances employed in dyeing and calico printing, with methods of examining and assaying these various bodies; also descriptions of apparatus and instruments used. The object of the authors has been to produce a book that would be of practical use in the laboratories of colour chemists, &c. Some of the subjects are considered in great detail; for example, the article on indigo occupies over 30 pages, while that on soap includes its composition, properties, manufacture, analysis, deter-

mination of melting and solidifying points, &c. Naturally, the coal-tar products receive a large share of attention. A. G. Green's scheme for the analytical determination of coal-tar dyes is given in full. There is also a good article on "The Analysis and Estimation of Arsenic in Textile Fabrics."

Arranged as a dictionary in alphabetical order, there is no index, but it is well printed, and occupies some 370 pages.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 18, October 28, 1901.

Chemical Reactions due to Radium.—M. Berthelot.—The author makes a series of experiments on a specimen of radium obtained from M. Curie. He compares certain specific chemical reactions, which are caused by light and by an electric current, to those reactions capable of being provoked by radium. These experiments are tedious, because of the very small quantities of radium able to be used and the necessity of working in glass envelopes. These latter absorb part of the rays, and, in certain cases, probably the most efficient portion; and they are also unsatisfactory on account of the long time necessary to accomplish these phenomena. The experiments tried were—(1). *The Action of Radium on Iodic Acid* (I_2O_5) *in Darkness.*—After nine days the acid begins to be tinted with violet, and after some time iodine vapour is apparent. (2). *Monohydrated Nitric Acid* (HNO_3).—At the end of two days the acid begins to discolour, whilst if kept for three years in total darkness it is still colourless. (3). A solution of octahedral sulphur in carbon disulphide, when exposed to light, deposits insoluble sulphur in virtue of an exothermic reaction; a tube of radium immersed in the solution in darkness produces no such effect. (4). Gaseous acetylene is very sensitive to the action of the electric current, an exothermic polymerisation taking place. This gas is not affected by either solar light or radium. (5). The slow oxidation of oxalic acid which takes place in presence of light, also takes place in the presence of radium.

Heat Evolved during the Reaction between Free Oxygen and Potassium Pyrogallate.—M. Berthelot.—During a course of electrolytic experiments, the author was led to measure the heat evolved during the action of free oxygen on pyrogallol in presence of potash. He dissolved the substances in molecular proportions and used equal volumes of the solutions. Through this mixture a current of oxygen was passed for some minutes. When O=16 gr., heat absorbed was +60·2 cals. Continuing the reaction, a second quantity (O=16 gr.) gave +50·0 cals. During the third experiment, +56·0 cals. was the number obtained. After this the absorption became too slow to carry on further measurements.

Separation of Iron.—Paul Nicolardot.—In 1859 Béchamp established the existence of soluble ferric oxychlorides to which he attributed the formula $Fe_2Cl_6(Fe_2O_3)n$. These compounds have an acid reaction, and in them it is impossible to detect either Cl or Fe by their usual reactions. Their sulphates are insoluble. Wyrouboff and Verneuil showed later that such compounds apparently exist for the metals of the rare earths, and that they form acid compounds of oxides, more or less condensed, whose sulphates are insoluble. The author revises Béchamp's work, and attempts the quantitative separation of the iron from such a compound. When a solution of neutral Fe_2Cl_6 is heated the liquid becomes darker, and if a boiling solution of a sulphate is added to this, a precipitate of a sulphate of condensed iron oxide is formed, whose composition varies according to the temperature and according to the dilution. If the sulphate of any metal, such as Mg, Zn, Cu, Ni, Co, Mn, Cd, Cr, Al, or ferrous sulphate is contained in the solution, the precipitate of iron contains no traces of the other metals.

Minimum Value of the Total Heat of Combination, Q.—M. de Forcrand.—The relation already given by the author (*Comptes Rendus*, cxxxii., p. 881) can be written $\frac{L+S}{T}=\frac{(l+s)M}{T}=\frac{Q}{T'}=\frac{L+S+q}{T'}=30$; Q being the sum of L, S, and q. From this relation various consequences follow directly. (1). At the moment of separation $\frac{L+S}{T}=30$ and $\frac{L+S+q}{T'}=30$; also $\frac{q}{\theta}=30$. θ being here the difference $T'-T$; θ and q are always positive. (2). When q tends towards zero, θ does likewise, and the relation $\frac{L+S}{T}=30$ again becomes apparent. It results, therefore, that the total heat of combination, Q, has for an inferior limit precisely L+S. The author has measured this for certain bodies.

Copper-aluminium Alloys.—Léon Guillet.—The author applies to copper-aluminium alloys a method which he has already described for those of tungsten and aluminium, and for those of molybdenum and aluminium. He was able to isolate the compounds of copper and aluminium predicted by the curve of fusibility and by metallographic researches. Three of these were obtained, corresponding to the formulæ Cu_3Al, CuAl, and Al_2Cu. The compound CuAl being obtained mixed with 2 to 3 per cent of a silicide of copper and aluminium.

Qualitative and Quantitative Determination of Traces of Antimony in presence of a Large Proportion of Arsenic.—G. Denigés.—The classical methods do not allow of the determination of very small quantities of antimony, especially in presence of relatively large quantities of arsenic. The author devises a method which allows of the estimation and detection of a thousandth of a milligrm., and even less, even when mixed with 500 times the quantity of arsenic.

No. 19, November 4, 1901.

Electrolysis of Ammonium Chloride Dissolved in Liquefied Ammonia.—Henri Moissan.—The electrolysis of ammonium chloride dissolved in liquid ammonia is performed in a glass vessel containing platinum electrodes. The ammonia gas is completely dried and freed from all possible impurities. When a current of 115 volts, and 30 ampères passes, no gas is evolved at the electrodes. After solution of the chloride the current easily passes, and gases are quickly evolved at the poles; chlorine being deposited at the positive pole, which colours the mass yellow. At this temperature, $-60°$ to $-80°$, no nitrogen is evolved, and no new ammonium chloride, as when the reaction takes place at ordinary temperatures, $4NH_3+3Cl=N+3NH_4Cl$. Hydrogen gas is evolved at the negative pole, and this is proved to be unmixed with other gases. The author shows satisfactorily that this difference in the reaction is merely due to the low temperature.

MEETINGS FOR THE WEEK.

Monday, 25th.—Society of Arts, 8. (Cantor Lectures). The Chemistry of Confectioners' Materials and Processes," by W. Jago, F.C.S., F.I.C.

Wednesday, 27th.—Society of Arts, 8. "Leather for Bookbinding," by J. Gordon Parker, Ph.D.

CHEMICAL AND PHYSICAL APPARATUS TRADE.

Wanted, Senior Assistant; also Junior.—State age, experience, and salary required, to Philip Harris & Co., Ltd., Birmingham.

THE CHEMICAL NEWS.

Vol. LXXXIV., No. 2192

THE SYSTEMATIC CHEMICAL TREATMENT OF RAGS FOR PAPER-MAKING.

By CLAYTON BEADLE.

The treatment of rags is almost universally looked upon, not only by the manufacturer, but also by the chemist responsible for their chemical treatment, as being entirely of an empirical order. Manufacturers do not regard such a material as rags as being amenable to any scientific treatment, although the manufacture of sulphite and soda wood-pulp is carried out in the most systematic and scientific manner. Having paid a great deal of attention to rag treatment for paper-making I have been led to the opposite conclusion. I am therefore writing this article with the object of showing that rags of all qualities, in spite of their peculiar nature and irregularity of composition, are amenable to as exact control and scientific treatment as almost any ordinary commercial product.

The difficulties that manufacturers of paper have to contend with are numerous. Although rags are purchased under well recognised trade names, the quality of each grade depends upon the idiosyncracies of each individual dealer. The dealer in turn is largely the victim of circumstances, as one might well infer from the fact that rags are merely the rejecta of civilisation. Each consignment must be carefully examined and valued on its own merits, independently of the trade name by which it is known. The paper-maker has then to sort the various rags he receives into twenty or thirty different qualities. By this means he is able to obtain fairly uniform qualities.

The chemical treatment of rags is merely for the purpose of removing the extraneous matter. This extraneous matter may best be described as consisting of all the dirt "that flesh is heir to." With these difficulties to face, it is hardly to be wondered at that the paper-makers make little use of scientific methods, and rely almost wholly upon their old rule-of-thumb methods and every-day observations.

The conditions under which rags are now treated in the best mills have been arrived at only after many years of observation. As good, if not better, results might have been arrived at after as many months almost, by pursuing a scientific method of investigation. In the ordinary method of procedure, rags of a given quality are dumped into a boiler with what is considered sufficient soda liquor, and, after a certain number of hours of treatment under steam pressure, the rags are washed and removed. If the result is considered good enough the conditions are repeated, but if the result is in any way unsatisfactory, one or other of the conditions is varied. It takes years by this plan of procedure to arrive at a point where no further improvement can be noticed.

The following is a practical and rapid procedure for arriving at the best conditions for boiling rags with soda which can be carried out by any ordinary works chemist:—One quality of rag is taken for investigation. The rags are filled into the boiler with a known quantity of soda. The capacity of boiler, the weight of rags, and the volume of liquor are noted. The charge should be as much as the boiler will take when "trodden in" after the liquor is added. The liquor should be just sufficient to insure complete saturation of rags, but no more. The time of bringing boiler to full pressure is noted. Samples of liquor are withdrawn every hour, and tested for "free" soda, and the boiling is continued until the free soda remains practically constant. The total soda is determined in the first and last sample, and in the case of a boiler heated with a steam-coil the total soda should remain constant throughout the boiling. When the rags are washed and removed from the boiler a sample is kept for comparison.

A second boiling is conducted on the same lines, but using soda only slightly in excess of that found to be consumed in the first trial. The boiling is continued until the free soda remains constant. The boiled rags should then be compared with the first trial, and the result should be practically the same. In order to ascertain the loss during treatment, ten pounds of rags, which must be so selected as to represent absolutely the bulk, are tied up in a loose bag made of coarse cheese-cloth. This bag is reclaimed after the boiling, and the contents of the bag are bone-dried, exposed to the air to air-dry, and weighed. From this the loss during boiling is calculated.

The examination of liquors taken during the boiling, to avoid unnecessary calculation and work, are treated as follows:—The liquor from each hour is placed in a marked bottle. The bottles are fitted into rough wooden boxes resembling cruet-stands, with leather straps for handles, which can easily be transported. Each box contains a series of bottles sufficient for a boiling. By this means samples from half a dozen boilings can be transported from boiler-house to laboratory by the chemist in one journey. From each sample 32 c.c. is withdrawn by means of a pipette made to measure this quantity. This is titrated with normal sulphuric acid until it no longer shows alkalinity when a drop is placed on a perfectly neutral non-absorbent litmus-paper. On account of the colour of liquor no indicator can be used in solution. For determination of total soda, 32 c.c. is evaporated down in a platinum dish, ignited, and the charred mass wetted with water, and again ignited. The soda can then be dissolved out with water and titrated without filtration in presence of methyl-orange. The readings on pipette give the percentage of Na_2O by dividing by 10. This method of determining the free and total soda has been checked by evaporating a quantity of the liquor to a solid mass, and examining for "free" soda by the method of "salting out." The two methods give almost identical results:—

Dilute liquor tested as above	28·5	per cent of total soda "free"
Concentrated and "salted out" ..	26·9	" " " " "

When once the conditions of boiling are fully established check tests can be done from time to time in a more simple manner, as follows:—A portion of the first and last sample is mixed in equal volumes, from which 32 c.c. is withdrawn, and total soda determined. Such quantity of each sample is then drawn off as to give reading on burette which, when divided by 10, represents percentage of "free" on "total" soda, without further calculation. The results are finally expressed in percentage of "free" soda on "total" soda. By examination of these figures the exact behaviour during boiling can be ascertained. I have found, moreover, that still further can be learned by plotting curves showing the diminution of "free" soda per hour during boiling, expressed as percentage on total "soda" present. The accompanying table shows the conditions arrived at after pursuing the mode of procedure above indicated. It must be remembered that no two mills have the same requirements, and there is no regular plan of procedure common to them all or to the majority of them. Furthermore, the different grades of rags in one mill are not comparable with those in another. The table cannot, therefore, be used as a guide for general practice, but merely as showing the mode of expressing the different factors of boiling, and by comparing them with curves constructed as above indicated an idea can be arrived at as to how the conditions influence the rate of absorption of soda. Curve No. 1 should show the absorption of soda per hour of different qualities of rags when treated under the conditions as shown in table. A dotted curve should be constructed from the mean of these. Curve No. 2 should

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.	17.	18.
Reference.	Quality of rag under treatment	Weight of charge, in cwts.	Gallons of liquor added per cwt.	Strength of cold liquor per cent Na_2O.	Percentage of Na_2O on rag.	Per cent free Na_2O in solution at different stages of boiling. Hours.						Free Na_2O at different stages of boiling when total $Na_2O = 100$. Hours.					
						0.	1.	2.	3.	4.	5.	0.	1.	2.	3.	4.	5.
90/8	No. 1 and No. 2 Cotton (mixed) ..	—	—	—	—	0·215	0·155	0·102	0·038	—	—	100	72	48	18	—	—
8/11	" " ..	32	24	0·33	0·697	0·22	0·083	0·033	0·017	—	—	100	38	15	8	—	—
24/8	No. 2 Cotton	—	25·7	0·654	1·68	0·54	0·26	0·13	0·10	—	—	100	48	24	19	—	—
67/8	No. 3 Cotton	—	22	0·90	1·78	0·60	0·35	0·16	0·10	—	—	100	60	27	17	—	—
73/8	"	—	24	0·70	1·50	0·50	0·245	0·155	0·085	—	—	100	49	31	17	—	—
80/8	"	—	25·2	0·55	1·22	0·35	0·245	0·152	0·068	0·036	—	100	70	43	13	10	—
15/11	"	31	24	0·65	1·36	0·42	0·13	0·09	0·065	—	—	100	31	21	15	—	—
26/11	"	30	25·5	0·76	1·74	0·60	0·255	0·180	0·150	—	—	100	43	30	25	—	—
86/8	No. 3 and No. 4 Cotton (mixed) ..	—	25	0·80	1·74	0·50	0·345	0·215	0·13	0·115	—	100	69	43	26	23	—
24/11	No. 2 Linen	32	24	1·17	2·45	0·73	0·18	0·145	0·14	—	—	100	25	20	19	—	—
63/8	No. 3 "	—	23	1·44	—	0·90	0·36	0·22	0·15	0·117	0·115	100	40	24	17	13	13
13/11	No. 2 and No. 3 Linen (mixed) ..	32	24	0·91	1·91	0·27	0·215	0·064	0·025	0·018	—	100	80	24	9	7	—
14/11	No. 3 Linens	32	24	1·0	2·14	0·60	0·30	0·12	0·09	0·065	—	100	50	20	15	11	—
56/8	No. 4 Linens	—	25·5	1·36	—	0·80	0·23	0·13	0·12	0·09	—	100	29	16	15	11	—
20/11	Cotton-waste (hulls)	—	28	1·76	4·40	1·08	0·345	0·304	0·260	0·245	0·230	100	32	28	24	22	21

show the absorption of soda per hour of No. 3 Linens when the conditions are varied as shown in table. A dotted curve constructed as the mean of No. 2 series is extremely regular, and gives a good idea as to how the rate of absorption of free soda should progress under favourable circumstances. Broad conclusions can be arrived at from a mean of all the curves which should hold good in a measure for all classes of rag-boiling. About one-half the total soda is neutralised at the end of the first hour, and after the third or fourth hour the chemical treatment has practically come to an end. Any further treatment is not only wasteful and unnecessary but harmful, as the rags go bad in colour. Many paper-makers are, however, treating for twelve to twenty hours, as they have no means of telling when the action is at an end. The amount of soda used also is merely a matter of guesswork. Some such system as I have outlined above should, I venture to think, be introduced into every paper mill where rag treatment is carried on on an extensive scale.

THE INFLUENCE OF MANURING ON THE CHEMICAL COMPOSITION OF POTATOES.

By WALTER F. SUTHERST, Ph.D.

It is well known that the quality of potatoes now-a-days is not so good as it was formerly, and it is thought that the large amount of fertilisers now added to force the crop has some influence in this direction, and though a much larger yield is obtained the quality suffers considerably, and it was the object of this investigation, carried out on the suggestion of Mr. R. P. Ward, Organising Secretary to the Cheshire County Council, to see whether the chemical composition of the potato was changed by the use of different manures.

The potatoes were planted in three plots a good distance apart. The first received no manure; the second 20 tons farmyard manure per acre; and the third, 5 cwts. superphosphate, 2 cwts. sulphate of ammonia, and 2 cwts. muriate of potash per acre; this part of the work being carried out most ably by Mr. W. Neild, F.R.H.S., Lecturer in Horticulture at the Agricultural College.

On taking up the potatoes, however, it was found that those in plot No. 3 were not anything like so numerous as expected from the high rate of manuring, and, on closer examination of the soil, the various salts added were still in the solid state; the extraordinary dry season not having wetted the soil sufficiently to dissolve them, and in that case could not be taken up by the plants. It will be seen from the analyses that this supposition is correct, for the composition of the unmanured tubers is practically identical with those manured with the artificials.

The substances estimated in each kind were water, dry matter, starch, ash, nitrogen, potash, phosphoric acid, and lime, and the methods used were as follows:—About 2 kilos. were chosen from each plot, and, after cleaning, cut into slices; and from these, 25 grms. were taken and dried, first at 55° C., so as not to alter the starch, then finally at 110° C. till constant weight; the loss being calculated as water, the residue as dry matter. This dry mass was then incinerated at a low temperature, the charred residue being washed out with hot water twice to accelerate the incineration; then the washings and final residue evaporated to dryness on the water-bath, and then gently heated to dull redness and weighed.

After estimating the water in each sample, the slices were fixed on glass rods and suspended in a water-oven and dried at a temperature of 55° C., and with this the other ingredients were estimated after grinding to a powder in a coffee-mill.

The starch was estimated by taking 3 grms. of the dried substance, placing it in a Lintner's pressure bottle, then 100 c.c. water added, and the whole heated for eight hours in a glycerin bath at 108° C. The contents of the bottle

were washed out with hot water, made up to 200 c.c., 20 c.c. concentrated hydrochloric acid added, and the mixture then heated in a flask fitted with a reflux tube on the water-bath for three hours. At the end of this operation, the mixture was quickly cooled under water, nearly neutralised with caustic soda, and made up to 500 c.c. From this, 50 c.c. were pipetted off and run into a boiling solution containing 60 c.c. Fehling's solution diluted with 60 c.c. water, and the whole boiled for three minutes. The precipitated cuprous oxide was then filtered off by means of an Allihn's filter-tube, washed with water, then alcohol and ether, dried at 110°, and heated in a current of hydrogen. From the weight of copper found, the amount of starch was calculated by E. Wain's table ("König. Unters. d. Landw. Stoffe," p. 750). In another 3 grms. the nitrogen was determined by Kjeldahl's method, using a mixture of sulphuric acid and phosphorus pentoxide, together with a little mercury for the oxidation. For the analysis of the mineral constituents, the ash obtained by incinerating 25 grs. of the dried substance was dissolved in dilute hydrochloric acid and made up to 250 c.c. with water, and in 50 c.c. of this the potash was found by first removing the sulphates with barium chloride, then precipitating the metals other than potassium, sodium, and ammonium compounds with ammonia and ammonium oxalate, filtering, the filtrate evaporated to dryness, and heated gently to volatilise the ammonium compounds. The residue was then treated with hot water, filtered, and to the filtrate an excess of platinum chloride added, and the liquid evaporated again to dryness and the dried residue triturated with alcohol and brought on to a filter, and the residue washed with 95 per cent alcohol till the filtrate ran through colourless; it was then washed through by hot water into a weighed platinum basin, evaporated to dryness, and dried at 110° C. From the K_2PtCl_6 found, the amount of potash (K_2O) present was calculated. In 100 c.c. of the ash solution, the phosphoric acid was estimated by first precipitating with ammonium molybdate, filtering, dissolving the yellow precipitate in dilute ammonia, and precipitating finally with magnesia mixture.

In the remaining 100 c.c. the lime was estimated by the oxalate method after removing the phosphoric acid with sodium acetate and ferric chloride.

The following is the summary of results obtained :—

	1. Unmanured.	2. Twenty tons farmyard manure.	3. Five cwt. superphosphate, two cwt. murate of potash, and two cwt sulphate of ammonia.
H_2O	76·24	78·08	75·95
Dry matter ..	23·76	21·92	24·05
Starch	17·762	13·557	17·142
Ash	0·967	0·973	0·964
CaO	0·025	0·022	0·028
N	0·506	0·516	0·493
P_2O_5	0·124	0·147	0·121
K_2O	0·628	0·635	0·630

The above results show very slight difference between the unmanured and plot manured with artificials, which was anticipated when it was seen that the manurial salts used were still in the undissolved form. Whether this really was the cause of the similarity in composition or truly represents effect of high manuring is still then an open question ; but the amount of water and starch in the potatoes manured with farmyard manure differs very much from the amounts in the unmanured ones, and one would expect that, with increased manuring, especially with artificial manures, this difference would be much greater.

The experiments will be repeated next year, since the results obtained at present are not sufficiently certain to give a correct opinion on the subject.

The Agricultural College,
Holmes Chapel.

THE CHEMICAL SOCIETY.

The following is a copy of the Memorial recently sent to the President of the Chemical Society, together with a complete list of signatories thereto :—

To the President of the Chemical Society.

Sir,—We, the undersigned Fellows of the Chemical Society, respectfully request you to summon an Extraordinary General Meeting of the Society, at the earliest possible date, for the purpose of—

(1) Proposing a modification of By-Law XI., and
(2) Submitting a resolution.

We subjoin the terms of the proposed modification and resolution, and have the honour to remain,

Yours very faithfully,

(*Signed*)

T. H. Page.
E. C. Jee.
E. Goulding.
T. A. Henry.
G. S. Blake.
F. B. Power.
H. A. D. Jowett.
G. T. Moody.
W. A. Davis
G. Bousfield.
E. Horton.
H. B. Redman.
J. Moir.
W. J. Kemp.
G. S. Newth.
G. T. Morgan.
J. C. Philip.
Chapman Jones.
A. J. Bullen Cooper.
W. Robertson.
C. A. West.
W. H. Merlett.
H. C. H. Carpenter.
E. O. Courtman.
F. Stanley Kipping.
H. H. Robins.
W. R. Hodgkinson.
Bernard Dyer.
Edward Barralet.
Samuel Rideal.
T. A. Lawson.
R. J. Friswell.
H. Silvester.
T. H. Pope.
Thomas Royle.
D. A. Sutherland.
D. A. Louis.
H. P. Stevens.
F. J. M. Page.
S. G. Hall.
Bertram Blount.
Charles Watson.
C. E. Eastick.
Peter MacEwan.
J. Lewkowitsch.
J. Heron.
C. A. Kohn.
W. F. Reid.
Oscar Guttmann.
S. Dickson.
J. H. Millar.
S. Williamson.
Otto Rosenheim.
P. Schidrowitz.
O. Hehner.
J. F. Thorpe.
J. Hübner.
L. G. Radcliffe.
J. W. Hinchley.
C. E. Browne.
F. F. Renwick.
Albert Cooper.
B. V. Storr.
P. Gerald Sanford.
H. R. le Sueur.
S. J. Peachey.
W. A. Wayland.
A. W. Harvey.
H. F. Fermor.
A. H. Coote.
A. C. Chapman.
C. E. Beadwell.
E. Neumann.
H. Bailey.
F. H. Carr.
E. Haynes Jeffers.
T. FitzGibbon.
J. Wilson.
W. T. Gilles.
A. Guthrie.
W. P. Draper.
A. Lapworth.
D. Northall-Laurie.
J. T. Hewitt.
F. Dixon.
A. G. Bloxam.
E. M. Chapman.
K. J. P. Orton.
Godfrey Melland.
T. Slater Price.
E. F. Harrison.
J. E. Mackenzie.
J. V. Eyre.
F. Southerden.
W. A. Lethbridge.
G. G. Quinn.
W. T. B. Ridge.
L. P. Wilson.
H. Wulff Kinnersley.
W. A. Handcock.
A. Marshall.
W. Rintoul.
J. C. Burnham.
S. S. Napper.
W. F. Thomson.
E. W. Lewis.
W. B. Woodbridge.
B. S. Bull.
T. Tickle.
W. H. Lewis.
James Grant.
John Allan.
T. R. Duggan.
W. C. Reynolds.
W. H. Taylor.
H. C. Sayer.

It is proposed—

(1) On line 7 of By-Law XI. (page 21, fifth line from top), to delete the words "the Council" and insert in their place the words "an Extraordinary General Meeting of the Society";

The part of By-Law XI. would then read:—

"The specific days and hour of meeting to be determined by an Extraordinary General Meeting of the Society."

(2) To resolve that the Ordinary Meetings of the Society shall continue to take place, as heretofore, on Thursdays, at 8 p.m."

The President of the Society has fixed the Extraordinary General Meeting for Thursday, December 12th, at 8 p.m.

THE QUANTITATIVE SEPARATION AND DETERMINATION OF URANIUM.*

By EDWARD F. KERN.

(Continued from p. 254).

PART II.—THE DETERMINATION OF URANIUM (*continued*).

Precipitation of Uranium by Ammonium Dihydrogen Phosphate.

As the precipitates formed by disodium hydrogen phosphate were slimy and difficult to wash, it was suggested that possibly this difficulty could be overcome by means of an ammonium phosphate. The precipitant used was ammonium dihydrogen phosphate. The mode of procedure was the same as when disodium hydrogen phosphate was used.

To a solution containing 0·1925 grm. of uranium were added from 0·1 c.c. to 1·5 c.c. nitric acid (sp. gr. 1·42) and sufficient water to make 150 c.c. volume. The solution was brought to boiling, ammonia (sp. gr. 0·90) was added to neutral reaction, and from 1 c.c. to 10 c.c. in excess. The ammonium uranate which formed was taken into solution by the addition of 50 per cent acetic acid, and from 1 c.c. to 5 c.c. in excess. The solutions, then acid with acetic acid, were brought to boiling, and the uranium precipitated by an excess of a saturated solution of ammonium dihydrogen phosphate. The best precipitations, that is, those which were most crystalline and easiest to handle, were formed when about one and a half as much precipitant was added as was necessary for the precipitation. The solutions were boiled for half-an-hour, and the precipitate allowed to settle before filtering. The precipitates were washed three times by decantation, and three times on the filter with a hot dilute solution of ammonium chloride (2 grms. salt to 100 c.c. water). The addition of ammonium chloride or of chloroform to the solution was found unnecessary, as enough ammonium salts were already present. The precipitates which formed were pulverulent and crystalline, and were as readily filtered and washed as the precipitates of ammonium uranate.

The precipitates were dried, separated from the filter-paper, and the paper ignited in a porcelain crucible, after which the precipitate was added, and the ignition continued at "redness" for about five minutes. The crucible was allowed to cool, and the residue moistened with a few drops of nitric acid (sp. gr. 1·42). The mass was dried over a low flame, then re-ignited for from ten to twenty-five minutes at "low redness" over a Bunsen burner. The mass after this treatment, was in all cases a lemon-yellow colour. The crucibles were allowed to cool in a desiccator, and weighed.

The results obtained are given in Table VI.

The filtrates were evaporated and tested for uranium with potassium ferrocyanide. No uranium was indicated.

In several cases when the ignition was done at a temperature above "redness," the precipitate would invariably assume a green colour, especially where the residue was in contact with the crucible. Whenever this occurred, the mass was again moistened with nitric acid (sp. gr. 1·42), dried over a low flame, and re-ignited at "low redness." By this treatment the mass was oxidised to $(UO_2)_2P_2O_7$.

Several precipitates, after having been weighed as uranyl pyrophosphate, were re-ignited over a blast-lamp for about fifteen minutes. The residue, in all cases, after such treatment was entirely green, but when moistened with nitric acid (sp. gr. 1·42), and re-ignited at "low redness," always changed back to lemon-yellow uranyl pyrophosphate, and their weight was the same as the original weight.

Solution No. 15 was allowed to stand for six days before filtering. The appearance of the precipitate was the same as those which were filtered directly.

The weighing of uranium as uranyl ammonium phosphate ($UO_2.NH_4.PO_4$) was undertaken but without success. The filtering through Gooch crucibles was tried, but owing to the fineness of the precipitate this could not be done. After trying to filter six solutions in this manner, the idea of weighing uranium as uranyl ammonium phosphate was abandoned as impracticable.

The Volumetric Estimation of Uranium.

Belohoubeck (*Zeit. Anal. Chem.*, 1867, vi., 120; Sutton's "Volumetric Analysis, 1900, p. 375), in 1866, estimated uranium by reducing the solution in a flask with metallic zinc and sulphuric acid. For small amounts of uranium, he states that the reduction is complete in about fifteen minutes, while for larger quantities the time required is much longer. The solutions, after reduction, were diluted and titrated by a standard potassium permanganate solution, the standard of which was made on ferrous ammonium sulphate.

Uranium differs from iron, as regards reduction, in that it is not reduced by hydrogen sulphide. When mercuric salts are present the uranium is, however, reduced by this reagent (Dammer's "Handbuch der Anorg. Chemie," 1893, vol. iii., p. 686).

The permanganate used for titrating uranium solutions is standarised by iron, two atoms of iron corresponding to one of uranium.

The reaction (Mohr's "Lehrbuch der Chem.-Analyt. Titrirmethoden," p. 267) which occurs during the titration of sulphate solutions of uranium is:—

$$5U(SO_4)_2+2KMnO_4+2H_2SO_4+2H_2O=$$
$$=5(UO_2)SO_4+2MnSO_4+2KHSO_4+3H_2SO_4.$$

The reaction which occurs during the titration of ferrous solution is:—

$$10FeSO_4+2KMnO_4+8H_2SO_4=$$
$$=5Fe_2(SO_4)_3+2MnSO_4+K_2SO_4+8H_2O.$$

$5U(SO_4)_2$ is equivalent to $10FeSO_4$, or $1U=2Fe$.

The reduction of uranium by zinc and sulphuric acid corresponds to the change of UO_3 to UO_2 (Watts's "Chemical Dictionary," iv., 820.

Experimental.

The fact that iron is so easily, and, at the same time, accurately determined by means of potassium permanganate, and that uranium solutions can be reduced, and then oxidised by potassium permanganate, suggested that possibly, with a few modifications, the Belohoubeck method could be adapted to the technical assay of uranium ores.

In order to demonstrate the best means of reducing uranium solutions, several different reducing agents were employed, the results of which are given below:—

The first series of experiments was made by reducing the uranyl solution by means of zinc and sulphuric acid

* Contribution from the Havemeyer Laboratories of Columbia University. From the *Journal of the American Chemical Society*, xxiii., No. 10.

TABLE VI.—*Precipitation of Uranium by Ammonium Dihydrogen Phosphate.*

Expt No.	Approximate dilution.	Salts added.	Temperature of solution after precipitation.	Crucible in which ignited.	Time of ignition.	Weight of $(UO_2)_2P_2O_7$.	Uranium equivalent.	Theoretical amount of uranium taken.
	C.c.				Minutes.			
8.	150	NH_4NO_3 + $NH_4C_2H_3O_2$	Boiling-point, boiled for one hour	Porcelain	10	0·2879	0·1924	0·1925
9.	150	,,	Boiling-point, boiled for ten minutes	,,	15	0·2880	0·1924	0·1925
10.	200	,,	Boiling-point, boiled for three-quarters of an hour	,,	20	0·2881	0·1925	0·1925
11.	200	,,	,, ,,	,,	20	0·2879	0·1924	0·1925
12.	150	NH_4Cl + NH_4NO_3 + $NH_4C_2H_3O_2$	,, ,,	,,	25	0·2881	0·1925	0·1925
13.	150	NH_4NO_3 + $NH_4C_2H_3O_2$	,, ,,	,,	25	0·2883	0·1226	0·1925
14.	200	,,	,, ,,	,,	15	0·2879	0·1924	0·1925
15.	150	NH_4Cl + $NH_4C_2H_3O_2$	,, ,,	,,	15	0·2878	0·1923	0·1925
16.	150	,,	,, ,,	,,	15	0·2882	0·1926	0·1925

at boiling temperature, then by means of zinc and hydrochloric acid.

The second series was made by reducing the uranyl solution by means of strips of metallic aluminum, first in dilute sulphuric acid solutions, then in dilute hydrochloric acid solutions.

The third series was made by reducing the uranyl solutions by means of metallic magnesium, first in dilute sulphuric acid, then in dilute hydrochloric acid solutions.

The fourth series was made by passing the uranyl solutions through a long Jones's reductor.

The fifth series was made by reducing the uranyl solution by means of a strong solution of stannous chloride, and destroying the excess of stannous chloride by adding sufficient mercuric chloride, as in the Zimmerman-Reinhart method, so largely used for the estimation of iron.

The standard solution of potassium permanganate was made by dissolving 18·96 grms. of the salt in distilled water, and diluting it to 6 litres, thus making a 0·01 normal solution. The standard was obtained by titrating ferrous sulphate solutions, containing a known quantity of iron. 1 c.c. $KMnO_4$ = 0·00548 grm. iron.

The uranium standard was calculated from the iron standard by the proportion:—239·6 : 2(55·9) = x : 0·00548; x = 0·01076.

Two equivalents of iron correspond to one equivalent of uranium, or the iron standard multiplied by 2·1425 gives the uranium standard. In order to get the uranium standard in terms of U_3O_8, multiply the iron standard by 2·5243.

The standard of the permanganate solution was verified by taking a measured amount of standard uranium nitrate solution, and reducing it with about 50 grms. of pure zinc and sulphuric acid (30 c.c. sulphuric acid, sp. gr. 1·84, in 150 c.c. of solution). The solution was diluted to 500 c.c., and titrated. The results obtained agreed to the fifth decimal place with those of the iron titration.

(To be continued).

THE ACTION OF SODIUM THIOSULPHATE ON SOLUTIONS OF METALLIC SALTS AT HIGH TEMPERATURES AND PRESSURES.*

By JOHN T. NORTON, Jun.

(Concluded from p. 255).

Experiments with a Salt of Aluminum.

IN a series of experiments made according to the method of Chancel, the results of which are shown in Table II., the solution in water of a weighed portion of pure ammonium alum was treated with an excess of sodium thiosulphate, and boiled vigorously for periods varying from ten minutes to half-an-hour.

TABLE II.

	Amount of alum taken as Al_2O_3.	Amount of $Na_2S_2O_3$.	Al_2O_3 found.	Error.
	Grm.		Grm.	Grm.
1.	0·0537	Large excess	0·0471	0·0066 −
2.	0·0537	,, ,,	0·0397	0·0140 −
3.	0·1083	,, ,,	0·0931	0·0152 −
4.	0·1137	5 grms.	0·0979	0·0158 −
5.	0·1139	2 ,,	0·1002	0·0137 −

These results substantiate the observations of Gibbs (*loc. cit.*) and of Zimmerman (*loc. cit.*), and show clearly that the boiling of solutions of the aluminum salt and sodium thiosulphate for a reasonable time does not effect the complete precipitation of aluminum as the hydroxide.

Table III. shows the result of submitting solutions of ammonium alum treated with varying quantities of sodium thiosulphate to a pressure of 20 atmospheres in the digester. It usually required about forty minutes to raise the pressure to the limit set; but this limit once reached, the digester was allowed to cool slowly. The duration of an experiment was about two hours.

TABLE III.

Alum taken as Al_2O_3.	Amount of $Na_2S_2O_3$ used.	Al_2O_3 found.	Error.
Grm.	Grms.	Grm.	Grm.
0·0565	5	0·0633	0·0068 +
0·1132	10	0·1154	0·0022 +
0·1153	5	0·1186	0·0033 +
0·1128	3	0·1129	0·0001 +
0·1126	3	0·1142	0·0016 +
0·1128	2	0·1120	0·0008 −
0·1136	2	0·1121	0·0015 −
0·1128	2·5	0·1136	0·0008 +
0·1124	2·5	0·1127	0·0003 +
0·1134	2·25	0·1133	0·0001 −

This table shows that sodium thiosulphate precipitates aluminum completely as the hydroxide when pressure is employed. The high results seen in some of the experiments appear to be due to the difficulty of removing by ignition the large amounts of sulphur formed in the action, as well as to the salts mechanically included in the precipitate. The amounts of sulphur and contaminating salts present depend upon the amount of thiosulphate taken; therefore, this should be as small as possible, 2 to 3 grms. being sufficient to precipitate all the alumina in

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. xii., No. 68.

a grm. of alum. When the amount of thiosulphate is reasonably restricted the weights of alumina accord fairly well with the theory.

Experiments with a Salt of Chromium.

Up to the time of the completion of this work nothing appears to have been done upon the quantitative precipitation of chromium as the hydroxide by means of sodium thiosulphate. Slater (*loc. cit.*) and Rose ("Traite de Chimie Analytique," i., 479) make mention of the action of sodium thiosulphate upon chromic acid, bichromates, and neutral chromates, but give no quantitative data. Recently, however, F. Faktor (*Zeit. Anal. Chem.*, 1900, xxxix., 345) has studied the action of sodium thiosulphate on chromium compounds. This investigator has found that if aqueous solutions of potassium bichromate and sodium thiosulphate are boiled together, a brown precipitate of hydrated Cr_2O_3, CrO_3 separates out, and the liquid turns yellow owing to the formation of normal chromate. A solution of potassium chromate is unaffected by boiling with thiosulphate, but in presence of ammonium or of magnesium chloride the chromium is separated rapidly and completely in the same form as with the bichromate, and after continued boiling with an excess of thiosulphate all the chromium present is precipitated. Faktor also found that a solution of chromic chloride is completely decomposed by continued boiling with thiosulphate, chromic hydroxide and sulphur being precipitated.

In the experiments shown in Table IV. a weighed quantity of pure potassium bichromate was dissolved in water, a known amount of sodium thiosulphate added, and the whole submitted to a pressure of 20 atmospheres in the digester. After cooling, the precipitate was filtered off on an ashless paper, ignited, and weighed as Cr_2O_3.

TABLE IV.

	$K_2Cr_2O_7$ taken as Cr_2O_3.	Amount of $Na_2S_2O_6$.	Cr_2O_3 found.	Error.
	Grm.	Grm.	Grm.	Grm.
1.	0·1330	3·3	0·1341	0·0011+
2.	0·1330	2·5	0·1326	0·0004−
3.	0·1322	2·5	0·1318	0·0004+
4.	0·1303	2	0·1303	0·0000
5.	0·1301	2	0·1310	0·0009+
6.	0·1320	2	0·1322	0·0002+

The results of these experiments are very satisfactory, and show that under pressure sodium thiosulphate precipitates chromium rapidly and completely as the hydroxide. It is advisable to use as small a quantity of thiosulphate as possible in order to prevent the presence of much free sulphur in the precipitate.

Experiments with a Salt of Beryllium.

In experiments dealing with beryllium the salt used was the chloride, a certain amount of which was dissolved in water diluted to a litre, and the amount of beryllium present determined by precipitating with ammonia and weighing as the oxide. Measured quantities of this solution were drawn from a burette as required. When a solution of a salt of beryllium and sodium thiosulphate are merely boiled together, nearly all the beryllium remains in solution. It was expected that the use of pressure would throw out all the beryllium, but, curiously enough, when solutions of beryllium chloride and sodium thiosulphate were submitted in the digester to pressures ranging from 10 to 80 atmospheres, only a partial precipitation of the hydroxide took place.

Experiments with Salts of Zirconium.

To prepare a standard solution of the salt of zirconium it was found to be most convenient to heat the double fluoride of potassium and zirconium with sulphuric acid, evaporate to dryness in platinum, dissolve the zirconium sulphate remaining in water and enough sulphuric acid to prevent the precipitation of the basic salt, and dilute to standard volume. Measured portions of the solution were taken from a burette as required for the experiments. The presence, however, of so large an amount of sulphuric acid as was necessary to keep the zirconium salt in solution tends to decompose sodium thiosulphate so rapidly that it was found necessary to nearly neutralise the solution with ammonium carbonate before adding the sodium thiosulphate. The solution of zirconium sulphate was standardised by precipitating with ammonia and weighing as the oxide.

In experiment I. of Table V., the solutions of zirconium sulphate and sodium thiosulphate were boiled together for a few minutes and then the precipitate filtered off, ignited, and weighed as the oxide. In experiments 2 to 5 inclusive, similar solutions were submitted to a pressure of 20 atmospheres in the digester.

TABLE V.

	ZrO_2 taken.	$Na_2S_2O_3$ taken.	ZrO_2 found.	Error.
	Grm.	Grms.	Grm.	Grm.
1.	0·0658	3	0·0651	0·0007−
2.	0·0658	3	0·0676	0·0016+
3.	0·0666	M	0·0670	0·0004−
4.	0·0641	2	0·0648	0·0007+
5.	0·0641	2	0·0645	0·0004+

These results clearly show shat sodium thiosulphate precipitates zirconium completely as the hydroxide either with or without the aid of pressure.

Experiments with a Salt of Titanium.

The solution of the salt of titanium was obtained by treating the double fluoride of potassium and titanium with sulphuric acid, evaporating to dryness, and dissolving the residue in sulphuric acid and water. The solution was standardised by precipitating the titanium hydroxide with ammonia and then adding an excess of acid as recommended by Gooch (*Am. Chem. Journ.*, vii., 285). This method of procedure avoids the tendency to excessive weight observed when the titanium hydroxide is precipitated by ammonia in presence of salts of the alkalis.

In the following table is shown the effect of treating a solution of titanium sulphate with sodium thiosulphate. Experiment 1 was conducted by merely boiling a solution of the reagents named above, filtering off the precipitate, and weighing as the oxide. In Experiments 2 and 3 the solution of titanium sulphate and sodium thiosulphate was submitted to a pressure of 20 atmospheres in the digester.

TABLE VI.

	TiO_2 taken.	Na_2S_2O taken.	TiO_2 found.	Error.
	Grm.	Grms.	Grm.	Grm.
1.	0·0240	2	0·0237	0·0003−
2.	0·0240	2	0·0240	0·0000±
3.	0·0240	2	0·0240	0·0000±

These results show that titanium is completely precipitated by sodium thiosulphate either with or without the aid of pressure.

To recapitulate, I have shown that sodium thiosulphate will completely precipitate aluminum, chromium, zirconium, and titanium as the hydroxides with the aid of high temperature and pressure. Beryllium is only partially precipitated under similar conditions. Mere boiling for a reasonable time will not precipitate aluminum and chromium, but it is sufficient in the case of zirconium and titanium.

In conclusion, I wish to thank Prof. F. A. Gooch for his kind advice and assistance.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

THE following are abstracts of papers received during the vacation and published, or passed for publication, in the *Transactions* :—

129. "*Additional Notes on Dinitro-orthoanisidine. A Chemical Reaction in which one of the Products continues the same Reaction.*" By R. MELDOLA and J. V. EYRE.

The authors give further evidence in support of the constitutional formula assigned to the dinitroanisidine already described (*Proc.*, 1901, xvii., 131). The 3 : 4 : 6-triamino-anisole and the corresponding 3 : 4-diamino-6-acetamino-anisole both form azines on condensation with benzil, which are described. The view put forward (*loc. cit.*), that the eliminated nitro-group comes out in the form of nitrous acid, is confirmed by quantitative determinations of the amount of diazo oxide formed from known weights of dinitroanisidine in acetic acid solution with accurately titrated solutions of nitrite. The latter was added to the extent of one-fourth of the theoretical quantity required on the assumption that one molecule of dinitroanisidine requires one molecule of nitrite. In all cases the diazo-oxide produced, as determined by the quantity of azo-β-naphthol compound formed, was far in excess of that capable of being produced by the nitrite added, thus proving that the nitro-group eliminated by the nitrous acid continues the process of diazotisation.

130. "*Ethyl Sec-octyl Tartrate and its Dibenzoyl and Diacetyl Derivatives.*" By J. MCCRAE.

Diethyl tartrate and octyl alcohol when saturated in the cold with hydrochloric acid give ethyl octyl tartrate, which is purified by distillation and washing with water. By the action of excess of acid chloride on this mixed ester, the dibenzoyl and diacetyl derivatives have been prepared. The optical rotation of these compounds has been determined, and the author finds that the molecular rotations are similar to the constants for the corresponding diethyl tartrates. This is a confirmation of the rule suggested by Guye, namely, that when substitution is effected at a point sufficiently far removed from the asymmetric carbon atom, only a slight change in the rotation is produced.

131. "*The Esterification of 3-Nitrophthalic Acid.*" By A. MCKENZIE.

The esterification of 3-nitrophthalic acid does not proceed normally in accordance with V. Meyer's rule. The author has studied the action of amyl and methyl alcohols on 3-nitrophthalic acid and its anhydride, and shows that the isomeric α- and β-acid esters are formed on esterification, as well as the neutral ester in certain cases.

The compounds, 2-*iso*amyl-3-nitrophthalic acid and *d*-2-amyl-3-nitrophthalic acid are also described.

132. "*Derivatives of 3-Nitrotolyl-4-Hydrazine.*" By F. G. POPE and J. M. HIRD.

The *hydrochloride* was prepared by Meyer and Lecco's method, and forms orange-red plates or needles, m. p. 190—191° with decomposition. The free base forms red tufts of needles, m. p. 110°. The *pyruvic acid hydrazone* forms yellow needles, m. p. 203° with decomposition. The *ethyl ester* of the pyruvic hydrazone is obtained as small, yellow needles, m. p. 140°. The *semicarbazide* forms small, yellow needles, m. p. 201°, and gives a deep violet colouration with cold alcoholic potash. The following compounds have also been prepared :—*Salicylaldehyde hydrazone*, scarlet needles, m. p. 226°; *furfuraldehyde hydrazone*, red needles, m. p. 165—166°; *benzaldehyde hydrazone*, red needles, m. p. 166°; *phenylthiosemicarbazide*, tufts of golden-yellow needles, m. p. 188°; *allylthiosemicarbazide*, yellow needles, m. p. 168—170°; *acetyl-nitrotolyl hydrazine*, yellow needles, m. p. 161°.

133. "*The Constituents of the Sandarac Resins.*" By T. A. HENRY, D.Sc.

The sandarac of commerce is the naturally exuded resin of various species of *Callitris*, usually either *C. quadrivalvis* or *C. verrucosa*.

Both varieties of resin consist of a mixture of resin acids and terpenes separable by steam distillation. From the latter, *d-pinene* has been isolated and identified. The chief volatile constituent is a diterpene, boiling at 265°, $\mu_D = 1{\cdot}5215$, $[\alpha]_D = +55°$, which behaves like a saturated substance, forming no additive compounds with bromine, hydrogen chloride, or nitrosyl chloride. Two resin acids have been isolated and examined. One of these has the composition $C_{20}H_{30}O_2$ (m. p. =171°, b. p. 265°, 11 m.m.), and closely resembles in behaviour the isomeric d *pimaric acid* of Vesterberg (*Ber.*, 1885, xviii., 3331), but is optically inactive, and is therefore named *inactive pimaric acid*. On reduction with hydriodic acid, it gives a diterpene, $C_{20}H_{32}$. On oxidation with permanganate, pimaric acid yields acetic acid, and a crystalline substance melting at 206°, which is probably *trimellitic acid*.

The second resin of sandarac has not been obtained in a crystalline form, but the highly deliquescent sodium salt and the characteristic lactone have been prepared; from analyses of these, the formula of the free acid is probably $C_{30}H_{48}O_5$. For this substance, the name *callitrolic acid* has been retained. The acid is remarkably resistant to the action of reagents, being unattacked even by hot fumic nitric acid. When heated in a vacuum, it is decomposed with the formation of carbon dioxide, and a diterpene identical with that occurring naturally in the resin.

134. "*Condensation of Phenols with Esters of the Acetylene Series.*" Part VI. By S. RUHEMANN and E. WRAGG, B.A.

The authors have continued the research on the interaction of phenols with ethyl chlorofumarate and ethyl phenylpropiolate, using eugenol and *m*-xylenol. From the former phenol they obtained *ethyl eugenoxyfumarate* and the corresponding acid, from which they have not been able to prepare the pyrone-compound in a pure state. *m*-Xylenol reacts with ethyl chlorofumarate to form *ethyl-m-xylenoxyfumarate*, the acid of which, on treatment with concentrated sulphuric acid, yields 6 : 8-*dimethyl*-1 : 4-*benzopyrone* 2-*carboxylic acid* (m. p. 210° with decomposition). This, on heating, loses carbon dioxide, giving 6 : 8-*dimethyl*-1 : 4-*benzopyrone* (m. p. 80—81°). With ethyl phenylpropiolate *m* xylenol forms *ethyl* β-m-*xylenoxy-cinnamate*, which is hydrolysed by alcoholic potash to the acid. This yields, on heating, m-*xylenoxystyrene*, and is decomposed by sulphuric acid into carbon dioxide acetophenone, and *m*-xylenol.

The authors have attempted to ascertain whether only the phenyl group in the aryl ethers of the unsaturated hydroxy-acid prevents the condensation to the pyrone compound taking place, and have found that *β-phenoxy-crotonic acid*, $CH_3{\cdot}C(O{\cdot}C_6H_5){:}CH{\cdot}CO_2H$, on heating, loses carbon dioxide, and yields *β phenoxypropylene*, $CH_3{\cdot}C(O{\cdot}C_6H_5){:}CH_2$ (b. p. 170°), and with sulphuric acid it breaks up into carbon dioxide, acetone, and phenol. To determine whether the condensation to the 1 : 4-benzopyrone compound depends upon the configuration of the aryl ethers of the hydroxy-acid, the authors have treated ethyl β *iso*chlorocrotonate instead of its stereoisomeride with sodium phenolate; they find, however, that the same substance is formed as when ethyl β-chlorocrotonate is used.

135. "*The Hydrobromides of Undecylenic Acid.*" By J. WALKER and J. S. LUMSDEN.

When hydrobromic acid is added to undecylenic acid, a bromo-undecylic acid, m. p. 51°, is formed at the same time as Brunner's acid, m. p. 35°. It is shown that the former is ω-bromo-undecylic acid, $CH_2Br{\cdot}(CH_2)_9{\cdot}CO_2H$, and not Brunner's acid as was previously supposed.

136. "*Normal Decane-dicarboxylic Acid.*" By J. WALKER and J. S. LUMSDEN.

This acid was prepared by electrosynthesis from pimelic acid and was found to be identical with an acid prepared from ω-bromo-undecylic acid. The solubility in water

differs entirely from the solubility of the acids described by Nördlinger and Komppa.

137. "*Action of the Chlorides of Phosphorus on certain Aromatic Ethers of Glycerin.*" By D. R. Boyd.

The author has studied the behaviour of symmetrical diphenyl glycerol-ether and some similar compounds when treated with the pentachloride and trichloride of phosphorus respectively.

Phosphorus pentachloride with diphenyl-glycerol-ether yields β-chloro-trimethylene-glycol-diphenyl-ether, $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CHCl{\cdot}CH_2{\cdot}O{\cdot}C_6H_5$, m. p. 37°. Phosphorus trichloride and diphenyl-glycerol-ether give a product which, on treatment with water, yields glyceryl-diphenyl-ether-phosphorous acid,—

$$C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH(O{\cdot}P(OH)_2){\cdot}CH_2{\cdot}O{\cdot}C_6H_5,$$

m. p. 119—120°. Phenyl-*p*-tolyl-glycerol-ether, $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}O{\cdot}C_7H_7$, m. p. 73·5—76°, which is obtained by the action of phenyl-glycide ether on *p*-cresol, yields β-chloro-trimethylene-glycol-phenyl-*p*-tolyl ether, $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CHCl{\cdot}CH_2{\cdot}O{\cdot}C_7H_7$, m. p. 60°, and glycerol phenyl-*p*-tolyl-ether phosphorous acid,—

$$C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH(O{\cdot}P(OH)_2){\cdot}CH_2{\cdot}O{\cdot}C_7H_7,$$

m. p. 106—107°.

Further, di-*p*-tolyl-glycerol-ether yields β-chloro-trimethylene-glycol-di-*p*-tolyl ether,—

$$C_7H_7{\cdot}O\ CH_2{\cdot}CHCl{\cdot}CH_2{\cdot}O\ C_7H_7$$

m. p. 70°, and glyceryl-di-*p*-tolyl-ether-phosphorous acid, m. p. 111—112°.

138. "*The Autofermentation and Liquefaction of Pressed Yeast.*" By A. Harden and S. Rowland.

The time required for the liquefaction of pressed yeast is greatly diminished by rise of temperature, whilst the rate of evolution of carbon dioxide is greatly increased. The evolution of gas ceases as soon as the yeast becomes liquid, and hence is small at 50°, owing to the rapid liquefaction of the mass (one to one and a-half hours), whilst the total volumes evolved at 39° and 26° do not differ greatly although the times required for liquefaction are five and fifty-three hours respectively. At 14° the time required is sixteen days, the rate of evolution being extremely slow, and the total volume evolved about 75 per cent of that produced at 26°. Alcohol is produced simultaneously, the process being apparently a true alcoholic fermentation of the glycogen of the cell. Microscopic examination shows that as the evolution of gas proceeds the glycogen disappears, and the vacuole of the cell increases in size. Finally, the vacuolar contents are discharged, and the cell appears shrunken and irregular in outline, whilst the protoplasmic contents are highly granular.

In the presence of oxygen, a process of oxidation accompanies the evolution of carbon dioxide, a considerable rise of temperature being produced, and the total volume of carbon dioxide increased. When exposed to a continuous current of oxygen, a sample of yeast was found to lose 26 per cent of its carbon.

139. "*Non-existence of the So-called Suboxide of Phosphorus.*" Part II. By C. H. Burgess and D. L. Chapman.

Substances obtained according to the methods described by Michaelis and Pitsch (*Ann.*, 1899, cccx., 45) and Michaelis and v. Arend (*Ann.*, 1901, cccxiv., 259) have been prepared and analysed, and shown to contain such a large amount of hydrogen that they cannot be regarded as a suboxide, but as red phosphorus containing hydrogen compounds. The authors show that some of the analytical results of Michaelis and Pitsch indicate that the substances prepared by them contained water, and that the proof of the absence of hydrogen in the substance, described by them as a pure suboxide, is inconclusive.

As red phosphorus is easily soluble in aqueous alcoholic potash, with formation of a red solution, red phosphorus resembles in this respect the so-called sub-oxide.

The authors conclude that both the properties and the analytical results support the view that the substances hitherto described as sub-oxides of phosphorus are only impure forms of amorphous phosphorus.

140. "*The Action of Ammonia on Metals at High Temperatures.*" By G. T. Beilby and G. G. Henderson.

Platinum, gold, silver, copper, iron, nickel, and cobalt have been exposed to the action of ammonia at temperatures ranging from 400° to 900°. In every case the physical effect of the treatment was to disintegrate the metal completely, whilst a large proportion of the ammonia was resolved into its elements. The fracture of metals which have been exposed to this action is spongy or cellular; under the microscope the metal appears as if it had been suddenly cooled whilst in a state of active effervescence. The penetration of the ammonia molecules into the metal is remarkably quick if the conditions are favourable.

The authors believe that the physical effects which result from the action of ammonia upon metals at high temperatures are due to the alternate formation and dissociation of nitrides taking place between certain narrow limits of temperature, the reaction going in one direction or the other according as ammonia or hydrogen molecules preponderate in the gases which are in contact with the molecules of the metal at and below the surface. In several cases the formation of nitrides has been definitely proved. The absorption of small quantities of nitrogen by pure iron renders it hard and brittle like steel.

141. "*The Condensation of Benzil with Dibenzyl Ketone.*" By G. G. Henderson and R. H. Corstorphine, B.Sc.

Benzyl and dibenzyl ketone readily condense when warmed with excess of aqueous potash, and *tetraphenylcyclopentenolone* is produced. It melts at 208°, is readily soluble in benzene but only sparingly so in alcohol. It yields an *oxime*, m. p. 167°, which when heated in alcoholic solution with *p*-bromophenylhydrazine gives a crystalline *hydrazone* melting at 169°. The *acetyl* derivative melts at 218°. Tetraphenyl*cyclo*pentenolone quickly reduces potassium permanganate, does not combine with bromine, but is slowly converted into a very unstable *bromine* derivative. When cautiously oxidised in the cold with chromic anhydride dissolved in glacial acetic acid, tetraphenyl*cyclo*pentenolone gives benzoic acid and a neutral *compound*, $C_{28}H_{20}O_4$, possibly *iso*benzil,—

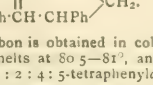
$$Ph{\cdot}C{\cdot}O{\cdot}COPh$$
$$\|$$
$$Ph{\cdot}C{\cdot}O{\cdot}COPh,$$

colourless crystals, m. p. 164—165°.

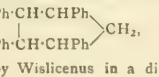
Tetraphenyl*cyclo*pentenolone undergoes partial reduction when boiled for an hour or two under a reflux condenser with hydriodic acid and red phosphorus, but the product is not tetraphenyl*cyclo*pentenone, but a *tetraphenylcyclopentenol*, which crystallises in colourless needles, m. p. 162°, is readily soluble in benzene, very sparingly so in alcohol; it quickly decolorises potassium permanganate in alkaline solution. It does not react either with hydroxylamine or with phenylhydrazine, but gives an *acetyl* derivative, colourless tablets, m. p. 181°. Bromine converts it into a *bromine* derivative, $C_{29}H_{22}BrOH$, colourless needles, m. p. 215°. By treatment with phosphorus pentachloride or alcoholic hydrogen chloride it yields a *mono-chlorotetraphenylcyclopentene*, $C_{29}H_{23}Cl$, colourless prisms, m. p. 181°.

When heated at 180° in a sealed tube with hydriodic acid and red phosphorus, tetraphenyl*cyclo*pentenol is reduced to two hydrocarbons, $C_{29}H_{24}$ and $C_{29}H_{26}$, which can be separated by means of ether, in which the former

is easily and the latter somewhat sparingly soluble. From its mode of formation the former is no doubt 1 : 2 : 4 : 5-*tetraphenylcyclopentene*,—



The other hydrocarbon is obtained in colourless crystals from alcohol. It melts at 80·5—81°, and is apparently identical with the 1 : 2 : 4 : 5-tetraphenyl*cyclo*pentane,—



already prepared by Wislicenus in a different manner. The former melts with decomposition at over 300°, and the latter at 80·5—81°.

142. "*The Chlorodibromo- and Dichlorobromo-benzenes.*" By W. H. HURTLEY, D.Sc.

Twelve tri-substituted chlorobromobenzenes should exist according to theory. The two symmetric compounds have been obtained by Hantzsch, Schleissing, and Jäger (*Ber.*, 1897, xxx., 2334), the 1-chloro-3 : 5-dibromobenzene from 3 : 5-dibromoaniline. The author has prepared all the twelve compounds from anilines of known constitution, many of which have not previously been obtained. The asymmetric compounds were prepared from dihalogen anilines, by replacing the amino-group by chlorine or bromine by Gattermann's method (*Ber.*, 1890, xxiii., 1222), and by eliminating the amino-group from asymmetric trihalogen anilines. The symmetric compounds resulted from the symmetric trihalogen anilines by eliminating the amino-group. The vicinal compounds were obtained from vicinal trihalogen anilines, also by eliminating the amino-group.

All the trichlorobromobenzenes are solids: the vicinal crystallise in well-defined rhombic plates; the symmetric, in long slender prisms; and the asymmetric in short thin prisms. All are very soluble in benzene, ether, chloroform, and petroleum, but less so in alcohol, from which they can be readily crystallised. The vicinal and symmetric compounds are easily volatile in steam, whilst the asymmetric are less so.

Asymmetric.—1 : 2-*dichloro*-4-*bromobenzene*, prisms, m. p. 24·5°, b. p. 237°; 1 : 3-*dichloro*-4-*bromobenzene*, prisms, m. p. 25°, b. p. 235°; 1 : 4-*dichloro*-2-*bromobenzene*, prisms, m. p. 33°, b. p. 235°; 1-*chloro*-3 : 4-*dibromobenzene*, prisms, m. p. 35·5, b. p. 256°; 1-*chloro*-2 : 4-*dibromobenzene*, prisms, m. p. 27°, b. p. 258°; 1-*chloro*-2 : 5-*dibromobenzene*, prisms, m. p. 40·5°, b. p. 259°.

Symmetric.—1 : 3-*dichloro*-5-*bromobenzene*, slender prisms, m. p. 77·5°, b. p. 232°; 1-*chloro*-3 : 5-*dibromobenzene*, slender prisms, m. p. 99·5°, b. p. 256°.

Vicinal.—1 : 2-*Dichloro*-3-*bromobenzene*, rhombic plates, m. p. 60°, b. p. 243°; 1 : 3-*dichloro*-2-*bromobenzene*, rhombic plates, m. p. 65°, b. p. 242°; 1-*chloro*-2 : 6-*dibromobenzene*, rhombic plates, m. p. 69·5°, b. p. 265°; 1-*chloro*-2 : 3-*dibromobenzene*, rhombic plates, m. p. 73·5°, b. p. 264°.

The following new anilines and anilides were also obtained:—3 : 6 *Dichloro* 4-*bromoaniline*, needles, m. p. 91°, and its *acetyl* derivative, prisms, m. p. 189°; 2 : 3-*dichloro*-4-*bromoaniline*, needles, m. p. 77·5, and its *acetyl* derivative, prisms, m. p. 138·5°; 2 : 4-*dichloro*-5-*bromoaniline*, flattened prisms, m. p. 86°, and its *acetyl* derivative, prisms, m. p. 192°; 2 : 4-*dichloro*-3-*bromoaniline*, plates, m. p. 78°, and its *acetyl* derivative, prisms, m. p. 138°; 3 : 5-*dichloro*-4-*bromoaniline*, needles, m. p. 129°, and its *acetyl* derivative, short prisms, m. p. 220°; 3-*chloro*-4 : 6-*dibromoacetanilide*, prisms, m. p. 174°; 3-*chloro*-2 : 4-*dibromoaniline*, plates, m. p. 88°, and its *acetyl* derivative, prisms, m. p. 152°; 2-*chloro*-4 : 5-*dibromoaniline*, flattened needles, m. p. 93°, and its *acetyl* derivative, needles, m. p. 193°; 2 *chloro*-3 : 4 *dibromoaniline*, plates, m. p. 91°, and its *acetyl* derivative, needles, m. p. 146°.

Extra Meeting, October 31st, 1901.

Prof. EMERSON REYNOLDS, Sc.D., F.R.S., President, in the Chair.

DR. ARMSTRONG delivered the

FRANKLAND MEMORIAL LECTURE.

Frankland was born at Churchtown, Lancashire, in January, 1825. When about seven years old he went with his mother and stepfather to Lancaster, where he lived until he entered Playfair's laboratory in 1840; he there attended a private school kept by a Mr. Willasey, until he was twelve years old, when he entered the Lancaster Grammar School in the lowest class, leaving it at the age of fifteen from the highest. His mother appears to have had a great influence in developing his scientific tastes, leading him as a child to pay attention to surrounding objects; these lessons were the means of causing him to seek information about natural phenomena for himself in books. Before he was twelve, he had read many books on chemistry, electricity, and magnetism, among others Priestley's Researches on Electricity. He thus learnt how to make a Volta's pile, with which he decomposed water; and having obtained a magnet, made most of the experiments of which he had read. His master appears to have encouraged him—for on hearing that he was showing experiments to his school-fellows, he invited him to bring his apparatus into the class room and demonstrate to the school. When about twelve years old he had a strong inclination for a mechanical trade, and having access to a cabinet-maker's workshop, acquired no slight skill. Mr. Willasey, however, dissuaded him, and awakened his ambition by telling him that he ought to aim at becoming a doctor; but as his parents were led to suppose that to give him a medical training was beyond their means, on leaving school he was apprenticed to a druggist in Lancaster. The six years he spent in this capacity were years of the hardest labour. His master not only never attempted to teach him anything, but did his best to hinder his scientific advance. But Frankland's ardour was not to be damped; by rising at four, he managed to get one hour and a-half for botanical work before the day's toil began. During the three years he was at the Lancaster Grammar School, he was able to carry on chemical experiments in a laboratory fitted up in the house of a school-friend; and as an apprentice he enjoyed the friendship of two men—Mr. Christopher Johnson, M.R.C.S., and Dr. James Johnson, who advised him what to read, and lent him apparatus, the latter even fitting up a laboratory in which Frankland and other druggists' apprentices in the town spent their evenings, Mr. Johnson occasionally telling them of Dalton's work, which was then going on.

It was on Mr. Johnson's advice that Frankland entered Playfair's laboratory in 1845. Playfair had then just been appointed organic chemist to the Government Department of Woods and Forests, of which the Geological Survey was a branch. Before six months had passed, Playfair made him his assistant at the College for Engineers, Putney; later on, early in 1847, he became Playfair's chief assistant. Meanwhile he had been offered the post of Professor of Chemistry in the Royal Agricultural College, Cirencester, and had decided to accept the office; but a difficulty arising, and acting on the advice of Kolbe, then one of Playfair's assistants, he decided instead to go to Germany. Kolbe and he went together to Marburg in May, 1847. In the autumn he returned to England to take up the position of lecturer on botany, chemistry, and geology at Queenwood College, Hants. There he met Tyndall, and so great was the ardour of the two young men that they rose at four and taught each other until eight o'clock before doing their work in the school. He returned to Germany again to work with Bunsen, in October, 1848, Tyndall, who at that time thought of becoming a chemist, accompanying him. He

took the degree of Ph.D in June, 1849, and shortly afterwards became engaged to Fräulein Fick, whom he married in 1851. In August, 1849, he went to Giessen to work in Liebig's laboratory. At Christmas he left for Berlin, intending to work with Rose, but receiving there the offer of the chair vacated by Playfair at the Putney College, he returned home. He remained at Putney until January, 1851, when he became Professor of Chemistry at Owens College, Manchester. In October, 1857, he returned to London as lecturer on chemistry in St. Bartholomew's Hospital. In 1863, he resigned this post to become Professor of Chemistry in the Royal Institution. In 1865, he succeeded Hofmann at the Royal College of Chemistry and Royal School of Mines, a post which he held until he retired in 1885. Meanwhile, in 1868, he had been appointed a member of the Rivers Pollution Commission. He died on August 9, 1899.

Frankland began research work with Kolbe very few months after entering Playfair's laboratory; before they left for Germany—within eighteen months of his having commenced to study chemistry systematically—they had completed their work on the hydrolysis of the nitriles, which led to the determination of the constitution of the great group of acids now known as carboxylic acids. They had begun to study the action of potassium on ethyl cyanide with a view to isolating ethyl; this work was completed in Marburg, and Frankland made his maiden appearance as reader of a paper before the Chemical Society in communicating the results which Kolbe and he had obtained. As soon as he was installed at Queenwood, he began independent work, and sought to isolate the alcohol radicles. On continuing this research, on the occasion of his second visit to Bunsen's laboratory, he soon succeeded in preparing "ethyl" and "methyl," and in the course of these experiments made the all-important discovery of zinc methyl and ethyl. The amyl compounds were studied in Liebig's laboratory. At Putney he continued his work on organo-metallic compounds; and it was here that he studied the action of chlorine on stannethyl, &c., and was first led to discover the law of valency; this work was completed at Manchester; the memoir in which Frankland formulated the doctrine which must hereafter always be associated with his name was read to the Royal Society on June 17, 1852.

Besides giving an account of Frankland's early education and subsequent career, and considering his character, Dr. Armstrong entered somewhat fully into an analysis of the work he did with Kolbe; he then proceeded to consider his investigations relating to the isolation of the hydrocarbon radicles, and his researches on the organometallic compounds, which culminated in the discovery of the doctrine of valency, leaving the vast mass of work—chemical and physical—which he did subsequently to be dealt with in the printed memoir. Attention was called to the great importance of Frankland and Kolbe's work on the acids of the acetic series. The two papers in which their results are described were referred to as deserving to rank as classics, as specimens of highly original and clearly reasoned precise argument, as well as on account of the importance of the results they disclosed. That they were in no way appreciated at the time of publication was due to the extraordinary hold which Gerhardt's type-system had obtained. For a like reason, Frankland's statement of the doctrine of valency produced originally but a slight impression, and it was only at a later stage —owing to the use that Kekulé had made of it in discussing the constitution of carbon compounds, benzene especially—that its importance became recognised, and it became the guiding principle; and even then Frankland's services were to a great extent overlooked. It was beyond the power of his contemporaries, in fact, to appreciate the bearings of his discoveries when they were first made known; and when the wave of Gerhardtism had spent its force, they appeared almost commonplace, so great had been the advance in knowledge meanwhile, and so insensibly had Frankland's ideas crept into their minds. Reasons were fully stated which appear to justify the belief that Kekulé must have derived his inspiration from Frankland, who alone is to be regarded as the discoverer of the doctrine of valency—Kekulé's great work having been to develope the consequences of its application to carbon compounds.

Taking the whole of Frankland's work into account, it constitutes a record which is altogether remarkable as evidence of his originality, of the catholic character of his interests, of his practical ability, and of his vigour; it must serve to place him in the very hightest rank among the chemists of the century, whilst his early work entitles him to be regarded as one of the great pioneers in establishing the modern doctrine of constitution.

On the motion of Professor Odling, seconded by Sir H. E. Roscoe, a vote of thanks was passsed to Dr. Armstrong for his lecture.

PHYSICAL SOCIETY.

Ordinary Meeting, November 22nd, 1901.

Prof. S. P. Thompson, President, in the Chair.

Prof. W. Cassie read a paper on "*Multiple Transmission Fixed Arm Spectroscopes.*"

The simplest form of spectroscope shown consisted of two half prisms, silvered on the back, between which a beam of light goes backwards and forwards with a slight upward inclination. The result in dispersing and resolving power is equivalent to direct transmission through a long train of prisms. The collimator and observing telescope are fixed, and adjustment is made by a double tangent screw which moves both the prisms. Two other types constructed on a similar principle were described, of which one had one prism and two speculum mirrors, and the other had two refracting prisms and a reflecting right angled prism. The adjustments of these instruments are simple, and their power great. By a small movement of an adjusting screw the observer can produce great changes of dispersion by passing from one to another of the series of spectra which are produced.

Prof. J. Perry asked if the third form of spectroscope, in which there is total internal reflection, had been tried experimentally. The amount of light lost at total internal reflection is much less than at reflection from mirrors, and he had found that the chief difficulty in using multiple reflections from mirrors was the great absorption of light.

Mr. T. H. Blakesley asked if there was any confusion due to overlapping of the spectra.

Mr. R. T. Glazebrook said he would like to know whether the author had any measure of the relative brightness of the first and last spectra.

Mr. W. F. Stanley said that by using three prisms instead of two it would be possible to substitute, in the first form of spectroscope, total internal reflection for normal reflection at a silvered surface.

The Chairman suggested a possible way of improving the third arrangement by using two prisms with their apices outwards, refracting at both foces, but not in the position of minimum deviation. Twenty-five years ago the present Astronomer Royal suggested the use of half-prism spectroscopes, and although they are often described in books they are seldom actually used. The advantage of using total internal reflection is well known, and is exemplified in binoculars, in some of which there are eight reflections from the object-glass to the eye-piece. He congratulated the author upon the mechanical arrangements used in his spectroscopes.

Prof. Cassie said that there was no confusion of spectra due to overlapping. With an ordinary Bunsen burner sodium flame a series of about five spectra are easily observed with dispersion equivalent to direct transmission through ten full-sized prisms. The loss of light at the reflections limits the number of transmissions that can be

used; but he believed that no other spectroscope with only two prisms would give dispersing power and resolving power in any way approaching the instrument described.

Prof. W. CASSIE then read a paper on "*The Measurement of Young's Modulus.*"

The apparatus described consisted of a horizontal needle (a bar of large moment of inertia), supported by a bifilar suspension made of the wire of which the stretch modulus is to be measured. The periods of the pitching, rolling, and bifilar oscillations of this system are observed, and an expression for the stretch modulus is obtained, which involves no measurements except the weight of the needle and the periods of the oscillations. The necessary adjustments, and the means of eliminating residual errors of adjustment, were described for two forms of the appatatus. One form also affords a simple means of statical measurement, by hanging a small weight on the needle at measured distances from the centre, calculating the difference of tension produced in the wires, and observing with a mirror and scale the consequent dip of the needle.

Dr. CHREE said that it would be possible to get a check on the theory by placing the movable weights at various positions on the needle, and observing the times of swing for pitching and bifilar vibrations. The ratio of the squares of these times should remain constant. It is difficult to say exactly what the apparatus measures, and he would like to see numerical results before expressing an opinion upon it.

Prof. J. PERRY said it would have been interesting to have had results from the apparatus so that they could be compared with those obtained by other methods. In the bifilar vibration there is a small twist in the wires, on account of which the torsional rigidity of the material affects the time of swing. He drew attention to the necessity of having the tensions in the two wires equal.

Mr. R. T. GLAZEBROOK, referring to the arrangement for clamping the bifilar at the top, pointed out that a small slip would modify the whole of the theory. An advantage of the apparatus lay in the fact that the wires used were shorter that those necessary in other methods. It was an interesting and ingenious application of theory to the methods of measuring Young's modulus.

Mr. WHIPPLE asked how the rolling and bifilar vibrations were experimentally separated.

Mr. A. CAMPBELL suggested that the difficulty of equality of tensions in the wires could be reduced by using longer wires a greater distance apart.

Prof. H. L. CALLENDAR said he had found that the torsional effect in a bifilar vibration was negligible, and that the flexure effect was not important. The absolute rigidity of the fastening at the top was the greatest difficulty.

Prof. CASSIE said his object had been rather to describe and exhibit the apparatus than give numerical results, although he had obtained numbers agreeing with those got by other methods. The mirrors for observing the vibrations were so placed upon the apparatus that each one was affected only by the particular vibration which it was designed to measure.

A paper entitled "*Notes on Gas-Thermometry*" (Part II.), by Dr. P. CHAPPUIS, was read by Dr. HARKER.

Messrs. Holborn and Day have published recently in a research on the air thermometer the results of a new determination of the expansion of Berlin porcelain between 0° and 1000°. The author has already drawn attention in a former note to the fact that part of the divergence found between the results of Callendar and Griffiths, and of Harker and himself, for the boiling-point of sulphur may be attributed to the uncertainty in the values assumed for the expansion of porcelain. In the present paper the author examines the way in which their results would be modified by the introduction of the dilatation deduced from the experiments of Messrs. Holborn and Day. It follows from the introduction of the new values that the boiling-point of sulphur deduced from experiments with a porcelain reservoir thermometer would be lowered from 445·2° to 444·7°, a number very close to that obtained by Callendar and Griffiths. In a second part of the paper Dr. Chappuis has re-calculated the divergences between the uncorrected nitrogen scale and the theoretical scale, and finds that the difference between these values and those given previously is too small to be of any practical importance.

The SECRETARY read a letter from Mr. A. E. TUTTON, in which he said that he was working at the expansion of porcelain, and hoped to present a communication to the Society shortly.

Prof. H. L. CALLENDAR said that he was highly gratified to see that the application of the correction for the expansion of the bulb of Dr. Chappuis's gas-thermometer, deduced from Holborn and Day's results, gave a value, 444·7°, for the boiling-point of sulphur in such close agreement with the value 444·5° deduced by Mr. Griffiths and himself in 1890. The agreement was really much closer than appeared at first sight, because the remaining difference of two-tenths of a degree in the results was almost exactly accounted for by the scale difference of the constant pressure and constant volume thermometers, according to the theory of Joule and Thomson. It was also interesting to remark that the corrected result found by Dr. Chappuis was in very close agreement with that deduced from their own observations by Messrs. Holborn and Day. Dr. Chappuis had not referred in the present note to the work of Bedford on the expansion of Bayeux porcelain, which he had criticised in a previous paper. A comparison of results would show that Bedford's results agreed very fairly, allowing for the difference of material, with Holborn and Day's, from 200° to 600° C.; and that both differed from those of Dr. Chappuis between 0° and 80°, when extrapolated, in a precisely similar manner. It was quite possible, as he (Prof. Callendar) had previously suggested, that the expansion of porcelain between 0° and 100° was anomalous. It appeared certain that some anomaly in the expansion at 800° was indicated both in the experiments of Bedford and also in those of Holborn and Day. It was also clear that Dr. Chappuis's results for Bayeux porcelain when extrapolated would agree with Bedford's at a temperature a little above 100° C., or very nearly at the same point at which his results for Berlin porcelain agreed with those of Holborn and Day.

Mr. R. T. GLAZEBROOK said he had felt for some time that it was of importance that the difference between the results of Callendar and Griffiths, and of Chappuis and Harker should be explained, and he was glad that the agreement was now so satisfactory.

The Society then adjourned until December 13th.

NOTICES OF BOOKS.

Blowpipe Analysis. By J. LANDAUER, Member of the Imperial Germany Academy of Naturalists. Authorised English Edition, by JAMES TAYLOR, B.Sc., A.R.S.M. London: Macmillan and Co. New York: The Macmillan Company. 1901.

THE third edition of this well-known text-book is not merely a reprint of that issued in 1892, but it brings the work quite up to date.

An interesting historical sketch of blowpipe analysis is given, taking the subject back to the year 1660, but its first actual application to chemical research appears to have been by Kunkel in 1679. Johann Gottibed Gahn, 1745—1818, was so skilled in its use that he could show the metallic copper from the ash of a quarter sheet of paper; and Berzelius, Plattner, Bunsen, Faraday, and Wollaston have all contributed to the progress of blowpipe analysis.

Many alterations have been made, and a good deal of new matter has been added to the text.

We notice a considerable extension of the details of flame colouration tests, and the use of the spectroscope; *wave-lengths* are given of the standard lines instead of the old meaningless scale divisions.

Tables of elements and atomic weights are given, but we are sorry to see they are faulty; didymium is included instead of neodymium and praseodymium.

The size and appearance of the book remain as before, and it is well indexed.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

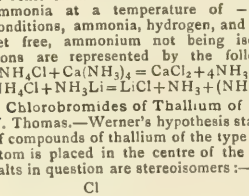
Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 19, November 4, 1901.

Chemical Effects produced by the Rays emitted by Radium.—Henri Becquerel.—Radiation from radium is composed of—(1) A portion deviable by the magnetic or electric field and identical with cathode rays; (2) a non-deviable portion, of which a fraction is very absorbable and the other portion exceedingly penetrating, thereby partially escaping measurement, owing to the difficulty of stopping it and transforming it into absorbable energy. The author examines the various chemical changes which occur, due to these portions, separately. M. and Mdme. Curie have already noticed the coloration effects produced on glass, porcelain, and paper. Amongst exothermic phenomena, the author now examines the transformation of white into red phosphorus under the influence of radium rays. A perceptible change takes place in twenty-four hours. Another action examined is the reduction of mercury bichloride in presence of oxalic acid. A precipitation of calomel is produced under the action of radium rays. Further experiments are described which were performed on germinating seeds under the action of radium.

Decomposition of Calcium-ammonium and of Lithium-ammonium by Ammonium Chloride.—Henri Moissan.—The discovery of the solubility of ammonium salts in ammonia led the author to undertake some new experiments with the liquefied gas. Calcium-ammonium, $Ca(NH_3)_4$, and lithium-ammonium, $Li.NH_3$, were allowed to react on a solution of ammonium chloride in liquid ammonia at a temperature of $-80°$. Under these conditions, ammonia, hydrogen, and the group NH_4 are set free, ammonium not being isolated. The reactions are represented by the following equations:—$2NH_4Cl+Ca(NH_3)_4 = CaCl_2+4NH_3+(2NH_3+2H)$ and $NH_4Cl+NH_3Li = LiCl+NH_3+(NH_3+H)$.

Chlorobromides of Thallium of the Type Tl_4X_6.—V. Thomas.—Werner's hypothesis states that in the case of compounds of thallium of the type Tl_4X_6, the thallium atom is placed in the centre of the group, and the two salts in question are stereoisomers:—



Mr. Cushman (*American Chemical Journal*, 1900, xxiv., 234) describes a method of preparation of these two isomers. The derivative α is stable, β being apparently characterised by its instability. The author repeats, with improved and altered details, all Mr. Cushman's experiments and draws certain interesting conclusions on the subject; these are described in detail in this paper.

Reactions of Trichloracetic Acid.—A. Clermont.—When equal numbers of molecules of alcohol and trichloracetic acid are mixed, and to this mixture a molecular proportion of monohydrated sulphuric acid is added, the heat evolved is considerable—sufficient to allow of the immediate formation of trichloracetic ether. After some minutes the liquid becomes opalescent, and after the addition of four times its volume of cold water, the drops coalesce and a distinct layer is formed composed of ethyltrichloracetic ether. This can be separated and washed, and, on the addition of its own volume of ammonia, is rapidly converted into trichloracetamide—a white crystalline body. This latter substance can be dried in the air and then sublimed, when it appears in brilliant plates and looks like naphthalene. These reactions, characteristic of trichloracetic acid, allow of its qualitative identification in a very short time.

Researches on the Isomerisations of Pinacone and its Derivatives.—Maurice Delacre.—The author's last researches on the question of the constitution of pinacoline led him to believe that the hitherto accepted formulæ are insufficient. He describes the experiments which led him to this belief, and states as a conclusion that it is more reasonable to admit that pinacoline is a mixture, but not a mixture in the sense that is usually attributed to this term. It corresponds to a state of equilibrium between the two formulæ $(CH_3)_3\,C.CO.CH_3$ and $\begin{matrix}(CH_3)_2C—C(CH_3)_2\\ \diagdown\quad\diagup\\ \quad O\end{matrix}$, and therefore preserves its claim to a chemical individuality.

Constitution of Piceol.—Ernest Charon and Démétrius Zamanos.—M. Tanret extracted from *Pinus picea* a glucoside (picein) decomposable by acids into glucose and piceol. He gives the empirical formula $C_8H_8O_2$ to piceol. The author, on examining this formula, believes it to be exactly that of a mono-oxyacetophenone, and such a hypothesis would explain the presence of the second oxygen atom in the molecule. His researches, which are described in this paper, demonstrate the correctness of this hypothesis. He prepares paraoxyacetophenone by other methods, and, using this and M. Tanret's piceol for various reactions, proves their identity.

MISCELLANEOUS.

Free Ammonia.—An ingenious and simple method of testing for free ammonia gas has lately been introduced by Mr. George Cockcroft, of Guy's Hospital. Many nitrogenous organic compounds when refluxed with caustic soda give off ammonia gas, which, as it is often accompanied by other vapours (volatile spirit, &c.) which disguise the characteristic odour, is not easy to recognise in small quantity. Mr. Cockcroft's method consists in using filter-papers soaked in a 7 per cent solution of $CuSO_4$. One of these while still slightly moist is placed in the open end of the condenser at the beginning of the reflux distillation. The evolution of even slight traces of ammonia can then be detected by the appearance of a dark blue colour on the paper ("ammoniacal" copper sulphate). This is unlikely to be vitiated by other vapours, and the method is, under these conditions, less troublesome, more delicate, and more conclusive than tests by odour, fuming with HCl, &c.

MEETINGS FOR THE WEEK.

Monday, Dec. 2nd.—Society of Chemical Industry, 8. "The Lemon Oil Industry," by Herbert E. Burgess and J. F. Child. "The Separation of Materials of different Specific Gravity," by J. W. Hinchley.

Royal Institution, 5. General Monthly Meeting.

Thursday, 5th.—Chemical, 8. Ballot for the Election of Fellows. "Influence of Substitution on the Formation of Diazoamines and Amino-azo-compounds," by G. T. Morgan. "The Determination of Available Plant Food in Soils by the Use of Dilute Solvents," by A. D. Hall and F. J. Plymen. "Some New Derivatives of Gallic Acid," by F. B. Power and F. Shedden.

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VOLUMETRIC ESTIMATION OF MANGANESE.

By HUGH RAMAGE, B.A., A.R.C.Sc I.

It is gratifying to learn from the opening paragraph of Messrs. Ibbotson and Brearley's paper (Chemical News, vol. lxxxiv. p. 247) that they have found the bismuthate method very satisfactory in practice. It is interesting also to learn that the rare metals, now used in the manufacture of certain special steels, do not interfere when present only in small quantities. Mr. Reddrop and the author did not anticipate the use of these rare metals. It is impossible to devise a rapid method of analysis which will apply, without modification, to all samples. The products of Sheffield include steels of all kinds, while we worked largely with mild steel and pig-iron.

It is unfortunate that only one of the points raised in Messrs. Ibbotson and Brearley's paper was dealt with, and that only partially, in the correspondence to which they refer. Some points mentioned in their paper must now be considered.

The original paper, by Mr. Reddrop and the present author, described one volumetric method for the analysis of wrought-iron, steel, and pig-iron. Messrs. Ibbotson and Brearley now refer to this as two processes, and include as a second the method of filtration, &c., employed in the analysis of ferromanganese and spiegel. There is no warrant for this in our paper. The original method gives accurate results when our instructions are followed (Chemical News, vol. lxxxiv., pp. 209—210). The two methods of collecting the filtrate were fully discussed in 1891. As stated in my recent paper, we obtained results in close agreement with one another by both methods. This was evidently because we added only a slight excess of hydrogen peroxide, and, consequently, at the end of the filtration, the full quantity of ferric nitrate was in presence of only a very small quantity of hydrogen peroxide. The reason given for the selection of the method described was most assuredly the one which influenced me most.

The assertion in the third paragraph is more serious, namely:—"The statement in this footnote is untrue." Messrs. Ibbotson and Brearley have missed the point of this footnote. It was added to explain why the time of filtration should not exceed fifteen minutes. This is perfectly clear in the paper, and the second sentence of the footnote, which is not quoted, is:—"Where a very accurate result is desired, the analysis should be completed without unnecessary delay." The decomposition referred to was the time reaction, and our statement was based on the results of experiments.

The addition of an excess of from 1·5 to 3·0 c.c. of hydrogen peroxide was recommended to correct the small error caused by the decomposition of the permanganic acid. A reference to the amount used in the more refined method described in my paper—a bare working excess—will make this clear. This point also has evidently been misunderstood. The decomposition referred to in this was found by our later experiments to be similar in amount in Farnley iron (which is almost free from carbon), and in steels containing up to 0·90 per cent of carbon. It does not therefore appear to be due to combined carbon. It appeared from some results obtained in a series of experiments made in the early months of this year, that combined carbon was a cause of low results. This was before our discovery of the initial reaction between hydrogen peroxide and ferric nitrate. We therefore oxidised the carbon by addition of sodium bismuthate to the hot solution. Mr. Ibbotson consented to receive—and did receive—a full report of this series of experiments about the end of April.

The more refined method described in my paper may be used in the analysis of all samples of steel and pig-iron in which—when the shorter method is used—the final reaction is unsatisfactory. It will not, however, be found necessary, nor of any advantage over this shorter method, in the analysis of the mild steels which constitute the great bulk of our commerce.

Messrs. Ibbotson and Brearley recommend ammonium ferrous sulphate, or ferrous sulphate, as a substitute for hydrogen peroxide. Mr. Reddrop and the author were unable to find a satisfactory substitute for that reagent; ferrous sulphate was regarded as unsuitable, because the solution of permanganic acid is always saturated with oxygen, and smells slightly of ozone. It was presumed that ferrous sulphate would be oxidised by the dissolved gas; this was tested experimentally, and the presumption confirmed. The following is copied from the original notes:—"Twenty c.c. dilute nitric acid stirred with 1 grm. sodium bismuthate and filtered into 5 c.c. ferrous sulphate solution, required 3·7 c.c. N/10 potassium permanganate; reaction *very* sluggish. Five c.c. ferrous sulphate alone required 4·1 c.c. N/10 potassium permanganate."

No results are quoted by Messrs. Ibbotson and Brearley in evidence of the accuracy of the modification they propose. It is important to remark in this connection that, in working out new methods of analysis, results given by other methods should not be taken as standards unless the errors of these methods are duly considered. The results quoted in my recent paper are compared with absolute standards, and the agreement is very close.

In comparing the cost of this method with the cost of other methods, it would be fairer to take into account the saving in wages and the cost of all the reagents. The sodium bismuthate may be economised in different ways, but a good excess must always be present, for it is a solid reagent. For this reason, also, it should be allowed at least three minutes to oxidise the manganese, &c.

With regard to the paper by Mr. Dutty, we considered the titration was more definite than a matching of tints. There is no reason, if great accuracy is not required, why the lead peroxide should not be replaced by sodium bismuthate in the ordinary colorimetric method. Filtration through asbestos would be much quicker than subsidence. This modification was suggested on two occasions in conversation with American chemists.

The experimental evidence before us is therefore in favour of the modifications of the bismuthate method recommended in our papers.

ACIDIMETRY OF PHOSPHORIC ACID BY MEANS OF BARYTA WATER.

By J. CAVALIER.

It is well known that if we titrate a solution of phosphoric acid with any given alkaline liquor, using methyl-orange or phthalein as indicators, the end-point of the first agent generally corresponds to the saturation of one atom of hydrogen of the PO_4H_3, and the end-point of the second to two atoms. This is the case with the alkalis, soda, and potash; the end-point of methyl-orange is correct, but that of phenolphthalein is not correct; by reason of the hydrolysis of the dimetallic phosphate we are not able to observe the change of colour very sharply, but a slow end point commences before the saturation of the second atom of hydrogen; this, however, is sufficient in the case of most titrations (Joly, *Comptes Rendus*, vol. cii., p. 317).

The results are very variable with the alkaline earthy bases; they depend not only on the dilution, but also on the manner in which the operation is conducted, and above all on the nature of the base.

I propose to examine the exact conditions necessary for

the use of the alkaline earths in the titration of free PO_4H_3, and, if it is possible, to detect the corresponding end-point of saturation of the three degrees of acidity.

The results given were obtained with baryta.

End-point with Methyl orange.—If to a phosphoric solution (1 litre = ¼th PO_4H_3) we add baryta water of moderate strength (1 litre = $\frac{1}{10}$th BaO), the end-point with methyl-orange is good, the solution remains clear, the rose tint passes in a continuous manner to orange, and then becomes suddenly pale yellow; with a little practice this change can be observed very accurately; it corresponds to the addition of half a molecule of the base to 1 molecule of PO_4H_3 (the actual figures found were between 0·497 and 0·505).

A more concentrated solution ($\frac{1}{10}$th) produces a gelatinous precipitate which re-dissolves in the acid liquor; it is important that this dissolution be complete at the moment of reading the end-point, otherwise the results will be too high; this can be effected by stirring or shaking sufficiently.

With a still greater concentration the complete resolution cannot be accomplished; we no longer obtain a solution at once limpid and neutral to methyl-orange, and the end-point can no longer be determined.

The neutral, clear solution obtained with a medium concentration contains $(PO_4H_2)_2Ba$, which decomposes spontaneously into PO_4H_3 and crystallised PO_4HBa; the solution becomes rose coloured again after standing for a few minutes. This transformation is the more complete, and the state of equilibrium corresponds to a more acid liquid, as the concentration is greater and the temperature higher (Viard, *Bull. Soc. Chim.*, Series 3, vol. xix., p. 749); but even with the $\frac{1}{10}$th solution it is not sufficiently rapid to interfere with the titration with methyl-orange.

The Use of Paranitrophenol as an Indicator.—Paranitrophenol, which is colourless in acid liquids, is yellow in an alkaline one. While Wieland (*Berichte*, vol. xvi., p. 1989) affirms that it is sensitive to CO_2, and is thus similar to phthalein, Spiegel (*Berichte*, vol. xxxiii., p. 2640) shows, on the other hand, that it can *always be used as an alternative to methyl-orange*, over which it has the advantage of a very marked end-point which is easy to recognise without very much practice.

I have found that it can be used very effectively for titrating acids with the alkaline carbonates, but the end-point is much less distinct than with the caustic alkalis; the saturation of the acid is complete on the appearance of a pale-yellow colour; the intensity of the colouration then increases if we continue to add carbonate.

The saturation of phosphoric acid by a caustic base (soda or baryta) in the presence of paranitrophenol (two drops of a 2·5 per cent weak alcoholic solution to about 20 c.c. of the liquid) gives an analogous end-point; the commencement corresponds (though rather later) with the end of the methyl-orange reaction:—

I. 10 c.c. PO_4H_3 (1 mol. = 1 litre) required in normal NaOH:—

Methyl-orange up to yellow colour	10·00 c.c.
p-Nitrophenol up to pale yellow colour ..	10·05 ,,

II. 10 c.c. PO_4H_3 ($\frac{1}{10}$th mol. = 1 litre) required in decinormal NaOH:—

Methyl-orange up to yellow colour	10·05 c.c.
p-Nitrophenol up to pale yellow colour ..	10·20 ,,

In the titration of phosphoric acid paranitrophenol can therefore be replaced by methyl-orange; the end-point is perhaps more easy to observe, but it is not quite so sensitive.

I might add that the greenish-yellow colour obtained does not interfere with the subsequent observation of the end-point of phthalein in the same solution.

End-point of Phthalein.—The figures in the following table show the amount of baryta (in molecules) which it is necessary to add to 1 molecule of acid to react with phthalein, while varying the conditions of the experiment.

	I. 1 litre = $\frac{1}{10}$ BaO. Mol.	II. 1 litre = $\frac{1}{20}$ BaO. Mol.	III. 1 litre = $\frac{1}{50}$ BaO. Mol.
The precipitate is entirely crystallised at the end of the operation carried out— In the cold	0·997	1·005	1·003
Hot	1·000	1·000	1·005
The precipitate is not entirely crystallised at the end-point. The total time of the titration being— ½ hour	1·17	1·08	—
1 min.	1·22	1·17	1·14
Less than 1 min.	1·35	1·19	1·15
The sudden addition of 1·5 BaO and back titration to decoloration of the phthalein— —	1·36	1·23	1·49
—	1·35	1·26	1·19

The nature of the end-point depends considerably on the method of conducting the operation.

It is very sharp when proceeding as recommended by Joly (*Comptes Rendus*, vol. cii., p. 378):—"The solution of baryta is run in until there is a distinct formation of a gelatinous precipitate; this consists of a tribarytic salt, which, on contact with the acid liquid, is transformed, either spontaneously or by stirring, into a crystalline precipitate of the bibarytic salt. By slowly adding baryta water we can obtain a fresh gelatinous precipitate which becomes transformed rapidly, and the operation is terminated when one drop of baryta gives an intense, persistent red colouration."

When the titration is carried out with baryta at 1/10th the length of the operation can be considerably shortened as follows:—The baryta is run in until the methyl-orange is just neutralised, and the clear solution is then heated; it rapidly gives an abundant crystalline precipitate, on contact with which the transformation is produced very quickly if we continue to add baryta.

With more dilute solutions the duration of the operation, which is practically the same hot or cold, is a little longer than in more concentrated solutions.

Whatever the dilution and temperature may be the precipitate can be obtained completely crystallised at the moment of the end-point, and therefore the latter is remarkably sharp; it requires, with great exactitude, the addition of 1 molecule of BaO (see the first two horizontal lines in the table).

The results are altogether different if the addition of baryta is made rapidly without waiting for the complete transformation of the gelatinous precipitate into the crystallised bibarytic one.

First of all, under these conditions, the end-point with phthalein is not distinct; we obtain transition tints with which it is impossible to observe a sharp change of colour. Then, at first the end-point is not persistent, the rose colour first obtained disappears in a few seconds on agitation. This should be compared with the observation made by Blarez (*Comptes Rendus*, vol. ciii., p. 265), that in the presence of a considerable amount of the base the quantity of baryta which combines with the phosphoric acid slowly increases with time.

The total amount of baryta which it is necessary to add to obtain an end-point persistent for some minutes, is always more than 1 molecule; the numbers found, evidently not very exact, are comprised between 1·08 and 1·25 molecules. The complete transformation into tribarytic phosphate requires 1·5 molecules. These figures become nearer to 1 as the stirring is more complete, the length of the operation greater, or the solution more dilute; all these conditions are precisely those which facilitate the formation of a crystalline precipitate.

We do not obtain any better result by suddenly adding 1·5 molecules of baryta to the phosphoric liquor (it is then strongly alkaline to phthalein), and then adding titrated

hydrochloric acid until the colour disappears. This shows the same characteristics as the direct titration; the end-point appears slowly, and after its first appearance the solution quickly returns to its red colour. On noting the moment when the decoloration persists for some minutes, the results found are higher than those given by direct titration with the same dilutions (1·19 to 1·36 molecules of BaO). But in no case, with the solutions used, do they approach 1·5 molecules, which corresponds with the total saturation of the three atoms of hydrogen in the PO_4H_3.—*Bull. Soc. Chim.*, Series 3, xxv., No. 16.

THE QUANTITATIVE SEPARATION AND DETERMINATION OF URANIUM.*

By EDWARD F. KERN.

(Continued from p. 261).

Part II.—The Determination of Uranium (*continued*).

Titration of Uranium Solutions with Potassium Permanganate.

Zimmerman (*Liebig's Ann. Chem.*, 1882, ccxiii., 300) recommends, when uranous solutions are titrated with standard potassium permanganate solution, that the permanganate be added in excess, and the excess then titrated back with a standard solution of ferrous sulphate. He stated that by this procedure the oxidation of the uranous solution by air is prevented. In the following titrations—about sixty in number, and also a number of others made later—the recommendation of Zimmerman was not observed, but the uranous solution was titrated in the same manner as a ferrous solution. The oxidation of the uranous solutions was prevented by placing about 1 grm. of dry sodium carbonate in the large Erlenmeyer flask in which the titrations were made. The mouth of the flask was closed by a 2½ inch funnel, and the solution which was reduced in a small Erlenmeyer flask was emptied into it. The solutions, which were quite acid, on coming in contact with the dry sodium carbonate, liberated carbon dioxide which filled the "titration flask," and prevented the oxidation of the uranous solutions.

The reductions, whether made by metallic zinc, aluminum, or magnesium, were made in a small 250 c.c Erlenmeyer flask, the mouth of which was closed by a small funnel. The uranyl solutions were poured into the flask, acidified, the metal added, and the reduction carried on at boiling temperature. After the reduction had occurred, the funnel and sides of the flask were washed down with distilled water, and the hot solution rapidly emptied into the "titration flask," which contained about 1 grm. of dry sodium carbonate. The flask in which the reduction was made was rinsed out four times with cold distilled water, the rinsings poured into the "titration flask," and the solution diluted to from 500 to 600 c.c. The titrations were made at once, adding the permanganate solution till pink "end-point," which was very delicate, when sulphate solutions were titrated.

The determinations were made as follows:—A measured amount of standard uranium nitrate solution was measured into a small beaker, and from 10 to 15 c.c. of sulphuric acid (sp. gr. 1·84), added. The solution was evaporated to dense white fumes, allowed to cool, then poured into an Erlenmeyer flask, which contained a small amount of water. The solution was diluted to a definite volume (100 to 200 c.c.), and more sulphuric acid added.

The best and most rapid reductions occurred when the amount of free sulphuric acid (sp. gr. 1·84) present was within the limits, 1 part acid to 4 parts solution, and 1 part acid to 5 parts solution. When the concentration is more than 1 to 4, the metal, especially zinc, is coated with a rather insoluble sulphate which retards the generation of hydrogen.

Comparing the time required for the complete reduction of uranyl solutions with that required for the reduction of iron solutions, it was found to be about twice as long, when equivalent amounts of uranium and iron salts were reduced.

When zinc was the metal used for generating the hydrogen, about 50 grms. of pure metal (15 lumps) were used.

When the solutions were reduced by means of aluminum, fifteen strips of the metal were used, size 8 m.m. wide by 15 m.m. long, and 0·5 m.m. thick.

The reductions by means of metallic magnesium were made by using eight pieces of a bar 8 m.m. in diameter and 15 m.m. long.

The reductions, whether made by means of metallic zinc, aluminum, or magnesium, were in all cases the same. The only difference noticed was the rapidity of solution of the metals; aluminum dissolved more rapidly than zinc, and magnesium more rapidly than aluminum. The reduction, whether carried on at boiling temperature for one hour, or for as long as five hours, did not go further than $U(SO_4)_2$. The time required for the reduction of about 0·1 grm. of uranium by zinc is about one hour, for about 0·2 grm. not less than one and a-half hours. The uranyl sulphate solution, at first yellow in colour, changes to light green, and finally to green with bluish tinge, having the appearance of a dilute solution of nickel chloride, which colour it retains even though the reduction be continued for as long as four hours.

The results, which were obtained by titrating uranous sulphate solutions, are all that can be desired, as they agree within analytical limits with those obtained by the standard gravimetric method, which is to precipitate the uranium with ammonia, and weigh it as U_3O_8.

The reduction of hydrochloric acid solutions was also tried. For this purpose, a measured amount of standard uranium nitrate solution was twice evaporated to dryness with 10 c.c. hydrochloric acid (sp. gr. 1·20). The dry mass of uranyl chloride was taken up with 15 c.c. hydrochloric acid (sp. gr. 1·20), and water added, after which the solution was poured into a small Erlenmeyer flask, and diluted to from 100 to 200 c.c. More hydrochloric acid was added, and the solutions reduced at boiling temperature in the same manner as the sulphate solutions. The reductions were made first by the use of metallic zinc, then by metallic aluminum, and lastly by metallic magnesium. In all cases where the reduction was carried on for from two to four hours, it approached (and in several cases reached) the sub-chloride (U_2Cl_6 or UCl_3). With solutions of about 100 c.c. volume and rather strongly acid (1 part hydrochloric acid, sp. gr. 1·20, to 4 parts solution), at boiling temperature the reduction to UCl_3 was complete within about two hours. By longer treatment the reduction went no further. The colour of the hydrochloric acid solution of uranium, at first yellow, changed to green, to bluish-green, to olive-green, and finally to reddish-brown—resembling the colour of old port wine. The solutions, previous to titration, were cooled by running water, diluted to about 600 c.c., and titrated in the same manner as the uranous sulphate solutions.

The "end-point" was not so delicate as when sulphate solutions were titrated. As no "preventative solution" was added, a small amount of chlorine was evolved after the solutions were allowed to remain standing for a few minutes. The interfetence of the "end-point" by chlorine was prevented by having a very small amount of free hydrochloric acid present, not over 3 per cent of the total solution.

The results are given in Table VII. (Experiments Nos. 1 to 27).

The reduction of uranyl solutions to the uranous state can also be made by passing the solution through a Jones reductor. The reductor used was much longer than those

* Contribution from the Havemeyer Laboratories of Columbia University. From the *Journal of the American Chemical Society*, xxiii., No. 10.

TABLE VII.

Experiment No.	Dilution at reduction.	Time of reduction.	Dilution at the time of titration.	Amount of free acid present.	Amount of $KMnO_4$ required.	Uranium equivalent.	Theoretical amount of uranium taken.
	C.c.	Hours.	C.c.	C.c.	C.c.		
				Reduction of Uranyl Solutions by Metallic Zinc.			
1.	100	2¾	600	15 H_2SO_4	13·10	0·15406	0·15400
2.	200	3	600	20 ,,	13·15	0·15464	0·15400
3.	125	1¼	500	20 ,,	8·20	0·09643	0·09625
4.	135	1½	500	25 ,,	8·20	0·09643	0·09625
5.	130	1	600	20 ,,	16·40	0·19286	0·19250
6.	130	1	600	20 ,,	16·35	0·19228	0·19250
7.	125	1½	500	20 ,,	19·60	0·23050	0·23100
8.	125	1½	500	25 ,,	19·65	0·23108	0·23100
9.	100	2½	600	30 HCl	21·10	—	0·15400
10.	200	2¾	600	25 ,,	19·80	—	0·15400
				Reduction of Uranyl Solutions by Metallic Aluminum.			
11.	110	½	600	15 H_2SO_4	13·15	0·15464	0·1540
12.	150	1½	600	20 ,,	13·05	0·15350	0·1540
13.	150	2½	600	20 ,,	13·10	0·15406	0·1540
14.	100	2¾	500	15 ,,	13·05	0·15350	0·1540
15.	100	3	500	15 ,,	13·10	0·15406	0·1540
16.	200	4	600	25 ,,	13·15	0·15464	0·1540
17.	120	1½	600	30 ,,	13·15	0·15464	0·1540
18.	200	2½	600	40 ,,	13·10	0·15406	0·1540
19.	200	2½	600	50 ,,	13·15	0·15464	0·1540
20.	75	1½	700	20 HCl	20·10	—	0·1540
21.	75	1½	700	20 ,,	18·85	—	0·1540
22.	200	3	700	20 ,,	17·40	—	0·1540
23.	200	3	700	20 ,,	19·60	—	0·1540
				Reduction of Uranyl Solutions by Metallic Magnesium.			
24.	125	1	600	20 H_2SO_4	13·10	0·15405	0·1540
25.	125	1	600	29 ,,	13·05	0·15347	0·1540
26.	125	2¼	700	20 HCl	16·90	—	0·1540
27.	125	2¼	700	20 ,,	17·60	—	0·1540
				Reduction of Uranyl Solutions by passing through Reductor.			
		Minutes.					
28.	100	9	600	20 H_2SO_4	8·20	0·09643	0·09625
29.	100	9	600	15 ,,	8·20	0·09643	0·09625
30.	110	10	500	10 ,,	13·15	0·15464	0·1540
31.	110	10	500	10 ,,	13·05	0·15347	0·1540
32.	115	11	500	15 ,,	13·10	0·15406	0·1540
33.	115	11	500	15 ,,	13·10	0·15406	0·1540
34.	120	12	500	20 ,,	13·10	0·15406	0·1540
35.	120	12	600	20 ,,	13·10	0·15406	0·1540
36.	100	10	500	20 ,,	16·40	0·19286	0·1925
37.	100	10	600	20 ,,	16·35	0·19228	0·1925
38.	125	12	600	25 ,,	26·20	0·30810	0·3080
39.	130	14	600	30 ,,	26·20	0·30810	0·3080
40.	150	18	600	35 ,,	26·20	0·30810	0·3080
41.	110	15	600	15 ,,	16·40	0·19286	0·1925
42.	115	18	600	20 ,,	16·40	0·19286	0·1925
43.	135	20	600	25 ,,	26·20	0·30810	0·3080

Solutions Nos. 41, 42, and 43 were twice passed through the reductor.

				Reduction of Uranyl Solutions by Stannous Chloride.			
44. 45. 46.	20	Minutes. ½	600	15	0·6—0·7	0·00823	0·1925
47. 48. 49.	75	½	500	20	0·8—1·5	0·01764	0·1925
50. 51.	75	½	500	20	0·4—0·6	0·00706	0·1925
52.	35	1	550	35	0·8	0·00941	0·1925
53.	50	1	550	45	2·0	0·02352	0·1925
54.	35	5	600	35	16·0	0·18816	0·1925
55.	50	5	600	45	18·5	0·21756	0·1925
56.	75	10	600	10	4·0	0·04704	0·1925
57.	75	10	600	10	8·5	0·09996	0·1925
58.	35	10	600	25	11·0	0·12936	0·1925
59.	30	10	600	15	15·5	0·18228	0·1925
60.	30	15	600	15	20·9	0·24578	0·1925

ordinarily employed for the reduction of iron solutions. It was made of a 50 c.c. burette, in the lower part of which was placed an inch layer of broken glass, and on top of this was poured an 18 inch column of 20 mesh amalgamated zinc. The amalgamation was done by washing the tube with a warm dilute solution of mercurous nitrate, then thoroughly washing it with warm distilled water.

The determinations were made by taking a measured amount of standard uranium nitrate solution, and evaporating it to dense white fumes with 10 c.c. sulphuric acid (sp. gr. 1·84). The solution was allowed to cool, then diluted to from 100 to 150 c.c., and more sulphuric acid added. The warm solution was poured through the reductor, and caught in a large Erlenmeyer flask, which contained about 1 grm. of dry sodium carbonate, and the mouth of which was closed by a small funnel. After all the solution had been emptied into the reductor, it was followed by about 250 c.c. distilled water. The solution was then diluted to 500 c.c., and titrated with 0·01 normal potassium permanganate solution to faint red end-reaction.

The time required for 100 c.c. of uranyl solution and 250 c.c. of water to pass through the reductor was about ten minutes; for 150 c.c. uranyl solution and 250 c.c. of water to pass through it required about twenty minutes.

Sutton ("Volumetric Analysis," under "Iron") states that while washing the reductor free from iron solutions, the wash-water should be kept above the zinc level, so as not to allow of any air-spaces between the successive additions of water, in which case hydrogen peroxide is formed, thus causing high results. This caution was observed in the reductions.

The most satisfactory results were obtained when the ratio of free sulphuric acid (sp. gr. 1·84) to total solution was not less than 1 to 6, nor more than 1 to 5. When the solutions contained more acid than the ratio of 1 to 5, the zinc sulphate which formed did not go into solution, and prevented the ready passage of the solution through the reductor. When the acid was present in amounts less than the ratio of 1 to 7, the reduction of the solution was incomplete, due to too slow action of the acid on the zinc. The reduction was complete in all cases when the ratio of free sulphuric acid (sp. gr. 1·84) to total solution was within the limits of 1 to 6 and 1 to 5. Even when the solutions were twice run through the reductor no further reduction occurred than when run through once.

The results obtained are shown in Table VII. (Experiments Nos. 28 to 43).

Reduction of Uranyl Solutions by Stannous Chloride.

These reductions were made in the same manner as iron by the Zimmerman-Reinhardt method. In some of the reductions the stannous chloride was allowed to act much longer than is ordinarily done for iron; but with the majority the procedure was the same as for iron reductions.

The colour of the uranyl chloride solutions was yellow, but on continued boiling with stannous chloride it changed to green, and, on still further boiling, to reddish-brown. When the solutions were boiled with stannous chloride, a small amount of dry sodium carbonate was added to the flask, the mouth closed by a small funnel, and the boiling continued.

When the reductions were allowed to continue for a minute or so, as for the reduction of ferric solutions, a very slight reduction occurred, but when the reduction was continued for from fifteen minutes to half-an hour, the reduction approached, and in several cases proceeded to the sub-chloride (UCl_3), the same as when a hydrochloric acid solution of uranium is reduced by either zinc, aluminium, or magnesium.

The uselessness of stannous chloride for the reduction of uranium solutions is shown in Table VII. (Experiments Nos. 44 to 60).

(To be continued)

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 7th, 1901.

Professor McLEOD, F.R.S., Vice-President, in the Chair.

MESSRS. W. Lowson, E. Neumann, A. Findlay, E. Horton, G. Tatam, G. W. F. Holroyd, and S. E. Sheppard were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frederick Thomas Allen, 15, Sea View Terrace, Hartlepool; Arthur Baker, 130, Walmersley Road, Bury, Lancashire; Walter Craven Ball, 19, Lewisham Hill, S.E.; Andrew Russell Bennet, 1, Wildman Street, Nottingham; Harding Bickford, 46, Currie Street, Adelaide, S. Australia; Henry Boyers, 20, Knox's Street, Sligo; William Burton, Cotleigh, Nunnery Fields, Canterbury; William Cormack, 3, Westfield Place, Eskbank, Midlothian; Frank Crossley, Duchy Bank, Seedley Road, Pendleton, Manchester; John Howard Davidson, Golden Hill, Stoke-on-Trent; Francis Davis, Whitwell, Elland, Yorks; Robert English, 8, Colwall Villas, Burley Road, Beckenham, Kent; Eugène Arthur Fasnacht, Clayton Mount, Newton Heath, Manchester; Henry Wippell Gadd, 42, Union Road, Exeter; Hermann Charles Thomas Gardner, London Hospital, E.; Edward Gillman, Barbados, West Indies; William Peer Groves, Oldfield Hall, Altrincham, Manchester; Herbert Harding, 20, Stratford Road, Kensington, W.; Beresford Ingram, 19, Lewisham Hill, Lewisham, S.E.; Walter Henry Jollyman, Spartan House, Colney Hatch Lane, Muswell Hill, N.; James David Kettle, 1, Vardens Road, St. John's Hill, S.W.; Julian Bruce, Kingsmill, Ordnance College, Woolwich; Alfred Tabois Larter, 184, Holland Park Avenue, W.; Peter Macdonald, Lapstone Road, Millom, Cumberland; Lewis Jenkin Meyrick, 137, City Road, Birmingham; Charles Killick Millard, The Gilroes, Groby Road, Leicester; Albert Edward Parkes, 43, Whitehorse Street, Stepney, E.; Charles James Tomlin Pollitt, Athole, Church Street, Croydon, Sydney, N.S.W.; Charles Leonard Royle, Nellikuppam, South Arcot, India; John Henry Ryffel, 10, Onslow Gardens, Highgate, N.; George Charlton Scott, Eston Grange, Grangetown, R.S.O., Yorks; Edward Charles Sherwood, 39, Vincent Square, Westminster, S.W.; Norman Smith, 15, King Street, Bury; William Henry Templeman, 67, Park Street, Spring Bank, Hull; Harold Fay Fleetwood Varley, 22, Strathblaine Road, New Wandsworth, S.W.; Herbert George Wallace, Axim, West Africa; Philip Lewington Whitehouse, 32, Lawrence Street, Dowanhill, Glasgow.

Of the following papers, those marked * were read:—

*143. "*Note on the supposed Formation of an Oxide of Hydrogen Higher than the Dioxide.*" By W. RAMSAY, F.R.S.

Bach (*Ber.*, 1900, xxxiii., 1506) has stated that evidence can be obtained of the existence of a peroxide of hydrogen higher than the dioxide by comparing the amount of oxygen evolved from peroxide on treatment with permanganate with the weight of the peroxide present in solution, as determined by titration with permanganate. It was suggested by Armstrong (*Proc.*, 1900, xvi., 154) that the discrepancy should be attributed to the formation of persulphuric acid and Caro's acid, due to the action of the peroxide on the sulphuric acid present during the titration. The author now showed that if peroxide be added to a mixture of sulphuric acid with permanganate, all the oxygen is evolved, but that if the permanganate be added to a mixture of peroxide with sulphuric acid, only a partial evolution of oxygen takes place, for neither persulphuric acid nor Caro's acid is readily attacked by permanganate. On the other hand, if acetic acid be substituted for sulphuric acid, the amount of oxygen evolved corresponds exactly with the amount of permanganate added, whether

the latter be added to a mixture of peroxide and acetic acid, or whether the peroxide be added to a mixture of permanganate and acetic acid.

*144. "*The Electrolytic Reduction of Nitrourea.*" By G. W. F. Holroyd.

Nitrourea can be reduced to semicarbazide much more easily if the reduction be effected by electrolysis than by the original method of Thiele and Heuser (*Ann.*, 1895, cclxxxviii., 311).

An aqueous solution of ammonium chloride serves as electrolyte. No porous cell is used. The reduction is effected at 20°. The poles are of iron or zinc. In the latter case an alternating current is employed to prevent the formation of a bridge of zinc from pole to pole. Four ampère-hours are required for the reduction of each grm. of nitrourea. The semicarbazide is precipitated as benzal-semicarbazone. The yield of re-crystallised benzalsemicarbazone is 60 per cent of the theoretical.

*145. "*The Constitution of Pilocarpine.*" Part III. By H. A. D. Jowett, D.Sc.

On a fuller examination of the products of the oxidation of *iso*pilocarpine with permanganate, it was found that, in addition to acetic and pilopic acids, small quantities of *propionic acid* and of a new acid named *homopilopic acid*, $C_8H_{12}O_4$, are formed. The formula $C_7H_{10}O_4$, previously proposed for pilopic acid, is confirmed both by analyses of various derivatives of the acid and by the determination of the molecular weight of the methyl ester.

Pilopic acid, $C_7H_{10}O_4$, melts at 104° (corr.) and is dextrorotatory $[\alpha]_D$ 15° = +36·1° in aqueous solution, with excess of alkali present $[\alpha]_D$ 17° = +3·2°. Its *methyl ester* boils at 155—160° under 10 m.m. pressure, and at 275° under 757 m.m. Its *barium salt*, $(C_7H_9O_4)_2Ba$, is a microcrystalline powder readily soluble in water. The *anilide*, $C_7H_9O_3NHPh$, forms white flat pearly plates melting at 110°. The *acid strychnine* salt, $C_{21}H_{22}O_2N_2$ $(C_7H_{10}O_4)_2$, is readily soluble in water and alcohol, sparingly soluble in ether, and melts at 120°. The *diamide* of the *hydroxy acid*, $C_7H_{14}O_3N_2$, formed by the action of ammonia on ethyl pilopate, occurs in acicular crystals, sparingly soluble in cold water or alcohol, freely soluble in these solvents when hot, and melts at 160°. The *barium* salt of the *hydroxy-acid*, $C_7H_{10}O_5Ba,H_2O$, is a microcrystalline powder freely soluble in water, $[\alpha]_D$ 15° = +6·1°. *Homopilopic acid*, $C_8H_{12}O_4$, boils at 235—237° under 20 m.m. pressure, and is dextrorotatory, $[\alpha]_D$ 21° = +45·4°, with excess of alkali $[\alpha]_D$ 21° = +5·9°. Titration of the acid showed it to be a monobasic lactonic acid. Its *ethyl ester* boils at 210° under 10 m.m. pressure. The *barium salt*, $(C_8H_{11}O_4)_2Ba$, is very hygroscopic. The *diamide* of the *hydroxy-acid*, $C_8H_{16}O_3N_2$, forms well-defined prisms melting at 208°, fairly soluble in hot water, but sparingly soluble in cold or hot alcohol or cold water. The *barium* salt of the *hydroxy-acid*, $C_8H_{12}O_5Ba,H_2O$, is a microcrystalline powder stable in the air. The author showed that the piluvic acid of Pinner and Kohlhammer (*Ber.*, 1901, xxxiv., 727) may possibly be a mixture of homopilopic with some pilopic acid. Repetition of previous experiments on the bromination of ethyl pilopate, giving rise to the formation of *iso*butyric acid, show that this acid is the product of a secondary reaction, and that the formula previously proposed (*Trans.*, 1900, lxxvii., 851) must be abandoned. Pilopic acid is not easily reduced by hydriodic acid, as no change occurs on heating to 210°.

Pilopic acid, when fused with potassium hydroxide at a high temperature, yields only one product—normal butyric acid. Fusion at a lower temperature produces a small quantity of a crystalline isomeric unsaturated acid melting at 190°, but the greater part of the acid is recovered unchanged.

Homopilopic acid on fusion with potash at a medium temperature, yields *α*-ethyltricarballylic acid, $C_8H_{12}O_6$.

From a consideration of the results obtained, the following formulæ are proposed for pilopic and homopilopic acids:—

$C_2H_5{\cdot}CH(CO{\cdot}O{\cdot}CH_2){-}CH{\cdot}CO_2H$ Pilopic acid.

$C_2H_5{\cdot}CH(CO{\cdot}O{\cdot}CH_2){-}CH{\cdot}CH_2{\cdot}CO_2H$ Homopilopic acid.

*146. "*A New Synthesis of α-Ethyltricarballylic Acid.*" By H. A. D. Jowett, D.Sc.

α-Ethyltricarballylic acid has been synthesised by the following reactions:—

1. *Ethyl-β-ethylcyanosuccinate* was prepared by condensing the sodium compound of ethyl cyanacetate with ethyl *α*-bromobutyrate (compare Bone and Sprankling, *Trans.*, 1899, lxxv., 839).

2. The sodium compound of ethyl *β*-ethylcyanosuccinate was condensed with ethyl bromoacetate with formation of ethyl *α*-ethyl-*β*-cyanotricarballylate. This reaction may be represented by the equation—

$$CH_2BrCO_2Et + CO_2Et{\cdot}C(CN)Na{\cdot}CH(C_2H_5){\cdot}CO_2Et = CO_2Et{\cdot}CH_2{\cdot}C(CN)(CO_2Et){\cdot}CH(C_2H_5){\cdot}CO_2Et + NaBr.$$

3. *Ethyl ethylcyanotricarballylate* was hydrolysed with sulphuric acid; the resulting acid, heated at 180°, gave *α*-ethyltricarballylic acid.

Ethyl β-ethylcyanosuccinate,—

$$CO_2Et{\cdot}C(CN)H{\cdot}CH(C_2H_5)(CO_2Et),$$

boils at 167—168° under 20 m.m. pressure, and has a density of 1·0647 at 15°/15°.

Ethyl α-ethyl-β-cyanotricarballylate,—

$$CO_2Et{\cdot}C(C_2H_5)H{\cdot}C(CN)(CO_2Et){\cdot}CH_2{\cdot}CO_2Et,$$

boils at 208° under 21 m.m. pressure, and has a density of 1·0972 at 16°/16°.

α-Ethyltricarballylic acid,—

$$CO_2H{\cdot}C(C_2H_5)H{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H,$$

melts at 157°, the figure previously given by Michael (*Ber.*, 1900, xxxiii., 3745). The following new derivatives have been prepared:—The *anhydro-acid*, $C_8H_{10}O_5$, could only be obtained amorphous, and yields an amorphous compound with aniline; the *triethyl ester* is a colourless limpid liquid boiling at 170—175°. The *barium* salt, $(C_8H_9O_6)_2Ba_3{\cdot}7H_2O$, is crystalline, and is more soluble in cold than in hot water. Only 6 molecules of water of crystallisation are lost at 180°. The *calcium* salt, $(C_8H_9O_6)_2Ca_3{\cdot}9H_2O$, is characteristic, as its aqueous solution, on heating to 100°, becomes a firm jelly which liquefies on cooling. The *copper* salt, $(C_8H_9O_6)_4Cu_3{\cdot}5H_2O$, is a greenish blue powder.

*147. "*The Benzoylation of Fatty Acids in the presence of Ammonia; Formation of Amides.*" By K. J. P. Orton.

On treating many monobasic fatty acids with excess of benzoyl chloride in the presence of ammonia and sodium hydroxide, the amides of the acids are formed together with benzamide. When methylamine is substituted for ammonia, methylamides are obtained. If the fatty acid and benzoyl chloride are heated together at 100—120° for two or three hours before treating with ammonia (or methylamine) and sodium hydroxide, the yield of amide is much increased and amounts in some cases to as much as 75 per cent of the acid used. When the acids possess hydroxyl or amino-groups, they are at the same time both benzoylated and converted into amides.

The following amides have been prepared by this method:—Phenylacetamide; *p*-nitrophenylacetamide; *p-nitrophenylacetmethylamide*, $C_6H_4NO_2{\cdot}CH_2{\cdot}CONHMe$, crystallises in long silky colourless needles (from water), m. p. 159°; *p-benzaminophenylacetamide*, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CONH_2$, prepared from *p*-aminophenylacetic acid, crystallises from alcohol in small plates, m. p. 248°; *p-benzaminophenylacetic acid*, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2H$, prepared by the Schotten-Baumann method, forms tufts of needles, m. p. 205—206°; *p-benzoxyphenylacetamide*, $C_6H_5{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}CH_2{\cdot}CONH_2$, prepared from *p*-hydroxyphenylacetic acid, forms insoluble microscopic crystals, m. p. 167—169°; *benzoylmandelic amide*,

$C_6H_5{\cdot}CH(O{\cdot}CO{\cdot}C_6H_5){\cdot}CONH_2$, prepared from mandelic acid, crystallises from water in tufts of silky needles, m. p. 162°; and *benzoylmandelic methylamide* in needles, m. p. 139°; *cinnamic methylamide*, $C_6H_5{\cdot}CH{:}CH{\cdot}CONHMe$, crystallises from water in plates, m. p. 111°; *dibromocinnamic methylamide* crystallises in lustrous prisms, which become coloured above 200°, melt and decompose at 214°. *Dibenzoyltyrosinnamide*, $C_6H_5{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(NH{\cdot}CO{\cdot}C_6H_5){\cdot}CONH_2$, prepared from tyrosin, crystallises in aggregates of lustrous needles, m. p. 246°. Stearic amide is obtained from stearic acid.

It is probable that either a compound anhydride of benzoic and the fatty acid (or possibly a simple anhydride of the fatty acid) is first formed; with ammonia (or methylamine) the anhydride yields the amide of the fatty acid.

•148. "*Liquid Nitrogen Peroxide as a Solvent.*" By P. F. Frankland, Ph.D., F.R.S., and R. C. Farmer, M.Sc., Ph.D.

A study of the properties of this liquid led to the following results:—Inorganic salts are not dissolved by nitrogen peroxide, and in most cases are unattacked. The liquid is a powerful solvent for organic compounds. It is a moderately inert reagent, but its activity is greatly increased by the presence of traces of water or of lower oxides. Most organic acids, as well as halogen and nitro-compounds and quinones, could be dissolved unchanged and recovered by evaporation. Hydroxy-compounds were generally, though not always attacked, phenol being converted to 2 : 4-dinitrophenol. Aniline derivatives were diazotised and some compounds were merely oxidised, as anthracene, which was completely converted into anthraquinone.

The electric conductivity of hydrochloric acid, as well as of a number of organic acids, was examined in this solvent, and found to be too small to be measured, showing that the liquid does not bring about electrolytic dissociation. A number of molecular weight determinations of dissolved substances were made by the ebullioscopic method. The constant for 1 grm.-molecule in 100 grms. of solvent was first determined by a series of experiments in which indifferent compounds (nitrobenzene, &c.) were used and found to be equal to 13·7. On extending the experiments to organic acids, these were found in many cases to be associated to double molecules. This was found to hold for acetic and benzoic acids and for several of their derivatives. Di- and tri-nitrophenol, on the other hand, gave their normal molecular weights.

•149. "*On an Incrustation from the Stone Gallery of St. Paul's Cathedral.*" By E. G. Clayton, F.I.C.

Around what is known as the Stone Gallery, at the base of the dome of St. Paul's Cathedral, is a balustrade of Portland stone, surmounted by a heavy coping-stone of the same material. Much of the surface of the stone is greatly "weathered," and is coated by a stratum of a grey or black substance, which in some places (especially on the under-side of the coping-stone) attains a thickness of three-quarters of an inch. This material, which is brittle and detachable with a knife, has a very rough and irregular surface, is stalagmitic in character, and, though differing in colour, in other respects resembles very closely some boiler deposits. It can easily be reduced to a fine grey powder, which, under the microscope, shows no morphological features indicating the presence of fungoid or similar matter.

Some of this incrustation has been analysed, with the following results (see Table, next column).

Evidently, therefore, the substance is composed chiefly of calcium sulphate, hydrated, together with some siliceous matter. Calcium carbonate, which might have been expected to be present, is not one of the constituents. What, then, is the origin of the incrustation? In the immediate vicinity, there is no obvious source of gypsum or plaster. It cannot have been blown upwards from the bare leaden roof of the Cathedral or floor of the gallery. The stones of the balustrade are cemented, of course, with mortar. Still less likely is it that so much calcium sulphate has found its way from the neighbouring thoroughfares. The sand and soot may, to a great extent, be thus derived, and perhaps a small proportion of the calcium sulphate represents coal-ash transported by wind. But after a careful consideration of all the circumstances, and especially the characteristic appearance of the incrustation, it is suggested that the presence of the main component is principally due to two centuries' solvent and weathering action of rain, charged with sulphurous and sulphuric acids derived from the gases and smoke of innumerable surrounding chimneys. The action exerted by rain beating heavily against the stone, in that exposed situation, must be very considerable. The deposit of calcium sulphate, left by the water dripping and running from the under-side of the coping-stone, has become gradually thicker, just as is the case with stalagmite and calcareous tufa, to which the external features of the incrustation give it a curiously close resemblance. That the weathering influence of rain has been potent, no one examining the surface of the Portland stone can have a moment's doubt.

In 100 parts by weight:—

Water lost at 100°	2·06
,, ,, 150	22·48
Organic matter (carbon)	1·10
Lime	26·44
Magnesia	0·27
Ferrous oxide	1·31
Silica, sand, &c. (Including combined silicic acid, SiO_2, 2·33)	10·39
Sulphuric acid (combined)	34·93
Phosphoric acid (combined)	1·02
Carbonic acid	none
Chlorine	trace
	100·00

Bases and radicles being combined, the composition is apparently as follows:—

Water (100°)	2·06
,, (150°)	22·48
Carbon (soot)	1·10
Calcium sulphate	59·38
,, phosphate	2·22
,, silicate	1·63
Magnesium silicate	0·67
Iron silicate	2·40
Sand and uncombined silica	8·06
	100·00

150. "*Note on Asbestos.*" By E. G. Clayton, F.I.C.

The following analyses of four kinds of asbestos (one of which, A, was stated to be of English origin, the remainder being examples of the ordinary mineral) are recorded for information and comparison, no published analysis of asbestos of English origin having been observed by the writer in any scientific journal.

Including the English specimen, all possess the general composition distinctive of true amphibole-asbestos, rather than asbestiform serpentine or chrysotile, which contains much more water and little or no lime. The English mineral consisted of moderately long, greyish-green fibres, easily separable, and in appearance resembling Italian asbestos, though characterised by unusual brittleness. B, C, and D, which had been pulverised before reaching the writer, were apparently associated with a little gypsum:—

	A.	B.	C.	D.
Water lost at 100°	1·19	0·87	0·86	—
,, ,, 150°	0·05	0·13	0·00	—
,, ,, a red heat..	0·70	0·95	1·83	—
Total water	1·94	1·95	2·69	1·39
Silica (with traces of manganese oxide, alkalis, &c.	60·88	48·48	59·82	61·74
Lime	11·11	6·19	5·91	6·91
Magnesia	10·84	35·52	28·27	25·72
Alumina	trace	4·69	1·25	2·30
Iron oxide..	15·23			
Sulphuric anhydride ..	—	3·17	2·06	1·94
	100·00	100·00	100·00	100·00

151. "*The Action of Nitric Acid on Methyl Dimethylacetoacetate.*" (Preliminary notice). By W. H. Perkin, Ph.D., F.R.S.

When methyl dimethylacetoacetate is heated with nitric acid of sp. gr. 1·4—1·45, vigorous action sets in, and if, when this has subsided, the product is thrown into water, a yellow oil separates, which on standing becomes semi-solid owing to the deposition of crystals. The crystalline product, when collected and purified by crystallisation from alcohol, melts at 65°, and gives numbers on analysis agreeing with those required for the formula $C_{14}H_{18}O_8N_2$. This new substance is decomposed by alkalis with formation of dimethylmalonic acid, *iso*-butyric acid, hydrogen cyanide, carbon dioxide, and ammonia, and when treated with ammonia gives dimethylmalonamide. Its composition appears to be expressed by the formula—

$$\begin{matrix} O{\cdot}N{:}C{\cdot}CO{\cdot}C(CH_3)_2{\cdot}CO_2CH_3 \\ | \quad\quad | \\ O{\cdot}N{:}C{\cdot}CO{\cdot}C(CH_3)_2{\cdot}CO_2CH_3 \end{matrix}.$$

It reacts with semicarbazide, yielding a crystalline substance of the composition $C_{16}H_{24}O_8N_8$.

When the substance melting at 65° is reduced with tin and hydrochloric acid, it yields two colourless substances melting at about 154° and 173°, as well as a third substance which melts at 177°, and crystallises in primrose-yellow needles.

The two colourless substances are isomeric, and have the composition $C_{14}H_{20}O_8N_2$; the one melting at 154° gives a crystalline condensation product on treatment with semicarbazide, whereas the other, melting at 173°, does not.

The primrose-yellow substance (m. p. 177°) has the formula $C_{13}H_{16}O_5N_2$, and is much less soluble in alcohol than the colourless reduction products. It combines with semicarbazide and with phenylhydrazine. It dissolves in potassium hydroxide, forming an intense orange-red solution from which a colourless, crystalline acid, $C_{12}H_{14}O_5N_2$, separates on adding a mineral acid. This acid melts at 214°, yields a well characterised barium salt, $(C_{12}H_{13}O_5N_2)_2Ba$, and is re-converted by treatment with methyl alcohol and hydrochloric acid into the primrose-yellow substance, which is therefore its methyl ester. The constitution of the three reduction products will be considered in the detailed paper.

Substances similar in constitution to that obtained by the action of nitric acid on methyl dimethylacetoacetate have already been prepared in the aromatic series; thus Hollemann (*Ber.*, 1895, xxviii., 3360) obtained diphenyldinitrosacyl,—

$$\begin{matrix} O{\cdot}N{:}C{\cdot}CO{\cdot}C_6H_5 \\ | \quad\quad | \\ O{\cdot}N{:}C{\cdot}CO{\cdot}C_6H_5 \end{matrix},$$

by the action of concentrated nitric acid on acetophenone. Baum (*Ber.*, 1895, xxviii., 3211) also obtained a condensation product of similar constitution by treating acetylmesitylene with nitric acid.

152. "*Note on the Displacement of Benzyl by Methyl in Substituted Nitrogen Compounds.*" By H. O. Jones, B.A., B.Sc.

In trying to effect the union of methyl iodide and dibenzylaniline, it was found that no action took place in the cold, but that on heating the mixture to 100° in a sealed tube only phenyltrimethylammonium iodide, unchanged dibenzylaniline, and benzyl iodide were obtained (*Proc. Camb. Phil. Soc.*, [2], xi., 114). On heating together dibenzylaniline and methyl iodide in the proportion of one molecule of the former to three of the latter to 100 for about two hours, a nearly theoretical yield of phenyltrimethylammonium iodide was obtained, the two benzyl groups having been eliminated as benzyl iodide.

It was of interest, in view of the fact that V. Meyer (*Ber.*, 1875, viii., 936) had shown that methyl iodide had no action on tetraethylammonium iodide, to see whether methyl iodide would displace the benzyl radicle in an ammonium compound. Phenylmethyldibenzylammonium iodide was, therefore, heated to 100° with methyl iodide, with the result that it was entirely converted into phenyltrimethylammonium iodide and benzyl iodide. The same displacement was effected in phenyldimethylammonium iodide and benzylaniline.

Experiments were made with ethyl, propyl, isobutyl, and allyl iodides on the above benzyl compounds; and with methyl iodide on other phenyl ammonium compounds; but at 100° no displacement was observed in any case.

The ready displacement of the benzyl radicle by methyl may be due to the "mobility" of the former, which is usually split off to some slight extent as iodide when a benzyl ammonium iodide is heated either in the dry state, or in aqueous or alcoholic solution, combined with the stability of phenyltrimethylammonium iodide, which is only decomposed at 220—225°. However, the non-displacement of benzyl by alkyl radicles other than methyl, and of such radicles as ethyl and propyl by methyl, suggests some peculiar relation (possibly stereo-chemical) existing only between the methyl and benzyl radicles.

NOTICES OF BOOKS.

Qualitative Chemical Analysis, Organic and Inorganic. By F. Mollwo Perkin, Ph.D. With Nine Illustrations and Spectrum Plate. London, New York, and Bombay: Longmans, Green, and Co. 1901. Pp. 266.

One of the great difficulties in teaching chemistry is to get a combination of a book-student and a laboratory-student; the one acquires the whole of his knowledge from reading, and is quite at sea in the laboratory, while the other is practically ignorant of theoretical principles. The ideal student would be one who combined the two characteristics, not neglecting one for the other. The author, recognising this difficulty, has endeavoured to write a book, in which theory and practice run, so to speak, side by side. He admits, however, that the book is more of a practical than a theoretical one.

The volume is divided into two parts; I. on Inorganic Analysis, and II. on Organic Analysis.

Part I. commences with the Dry Reactions, followed by a chapter on Reactions in Solutions. In Chapter III. the division of the metals into groups is explained, but the author has departed from the usual custom of giving the group numbers, i., ii., iii., &c., but, instead, with a view to preserving their individuality, he calls them by the name of a characteristic element; thus, instead of group i. or group iv., we have "the silver-group" and "the iron-group." The following chapters deal *seriatim* with these groups and with the acids, and this part is concluded with the necessary analytical tables for the detection and separation of the metallic and acid radicals.

Part II. commences with the Qualitative Elementary Analysis of Carbon Compounds, followed by others on Organic Acids and Phenols, Aldehydes, Alcohols, the Sugars, the Alkaloids, &c. In the summary it is truly

pointed out that organic analysis is far more complicated than inorganic work, there being no simple set of tables for the former as there are for the latter. Organic chemistry is so intimately bound up with theoretical questions that it behoves the student to give much more time to book work than is necessary in the other branch of chemical science.

The book is well and clearly written and printed, and contains an index of seven columns.

Elementary Organic Analysis. The Determination of Carbon and Hydrogen. By Francis Gano Benedict, Ph.D. Easton: The Chemical Publishing Company. Pp. 86.

But few elements are required to be determined in organic analysis, the most important being carbon, hydrogen, oxygen, and nitrogen; the latter being estimated by difference.

These operations require the minutest care and attention to detail to get anything like trustworthy results. Instructions with regard to these details are very often too vaguely given or hardly referred to at all in many text-books.

In the volume now before us the author expresses the hope that the descriptions of processes here recorded will aid in making this method of analysis more familiar and satisfactory.

After a preliminary description of the necessary apparatus and absorbing agents, &c., the author gives detailed instructions for performing the combustions of various bodies, such as those containing nitrogenous substances, the halogens, sulphur, liquids, and volatile bodies, &c.; and finally, the combustion of explosive bodies. The book concludes with the calculation of results, an appendix, and an index.

Thirty-seventh Annual Report on Alkali, &c., Works. By The Chief Inspector. Proceedings during the year 1900. London: Eyre and Spottiswoode. 1901. Pp. 144.

The number of works now registered under the Acts in England, Ireland, and Wales is 1054; of these 85 only are works decomposing salt; there are also 127 works registered in Scotland, bringing the total number of registered works to 1181. During the year, 4989 visits were made, and 5431 tests. It is to be regretted that as a result of these tests there has been no diminution in the number of prosecutions under the Act, the number being five.

The average escape of acids of sulphur and nitrogen from exits of sulphuric acid works throughout the country shows a slight reduction from that for 1899, though being a fraction higher than the similar figures for 1897 and 1898. In several cases this year the stock of acid in the vitriol chambers has been drawn down to the very minimum required to lute the gases. Under such conditions the chamber reactions themselves are liable to be rapidly affected, changes taking place with extreme rapidity in the direction of disorganisation of the process and increase of escape, and requiring the utmost vigilance on the part of the management to keep under control.

Through the courtesy of manufacturers the Chief Inspector has been enabled not only to continue the table given for several years past on the produce of ammonia from all sources in the United Kingdom, but, by the sanction of those engaged in the recovery of by-products from coke ovens, to make this table more instructive by the inclusion of a new sub-head—ammonia recovered from coke ovens; the growth of this industry has been comparatively rapid of late years, and several new plants have started operations this year.

The results of the examinations of the chimney gases for hydrochloric acid at salt works has been very satisfactory; the limit allowed is one-fifth of a grain per cubic foot of escaping gases; the average actual escape has only slightly exceeding one-quarter of this amount.

It is evident that taking it all round the alkali industry is in a very satisfactory condition, in so far as concerns the care taken and the skill with which the operations are conducted. It is, however, to be regretted that there has been one explosion attended with loss of life; this was due to the accumulation of a mixture of explosive gases in a tar-well at a gas works in Lancashire.

Researches on the Past and Present History of the Earth's Atmosphere. Including the Latest Discoveries and their Practical Applications. By Dr. Thomas Lamb Phipson. London: Charles Griffin and Co., Limited. 1901. Pp. 194.

The science of the atmosphere is very far-reaching, and includes in its wide embrace not only meteorology but also the realms of physical geography, geology, chemistry and physiology, &c.

The author commences his interesting treatise from the very earliest times, when the probabilities are that there was no free oxygen in the air. The first free oxygen was due to the action of plant-life, and after many ages the atmosphere became fit for the lowest forms of respiratory life; as time went on less and less carbonic acid was present, while the proportion of free oxygen continually increased, until, finally, the author proposes this seeming paradox, that oxygen, which is admitted to be the product of life whilst it is the condition of life, will perhaps by its final predominance be the cause of universal death.

The second part of this volume deals with the atmosphere of our present period, from various points of view, both as to chemical constitution; physical properties, such as the odour in different countries, at sea, on land after a summer shower, &c.; electric phenomena; solid substances, which either fall like meteorites, or can be detected in suspension, and a host of other important matter.

The book consists of twenty-four chapters, all of which teem with interesting information and speculation; the whole being written in the author's well-known chatty style, which needs no further commendation from us.

Besides a full table of contents there is also a good index.

Painters' Colours, Oils, and Varnishes. A Practical Manual. By George H. Hurst, F.C.S., Member of the Society of Chemical Industry; late Lecturer on the Technology of Painters' Colours, Oils, and Varnishes at the Municipal Technical School, Manchester. Third Edition, Revised and Enlarged. London: Charles Griffin and Co. Limited, Exeter Street, Strand. 1901.

The demand for this manual having rendered a third edition necessary, the author has taken the opportunity of adding many recently acquired details of colour manufacture, thus bringing the subject up to date. There is no need to enlarge upon the thoroughly sound and practical character of the work, having already done so upon the issue of previous editions. Colour and varnish makers are to be congratulated upon having had the subject of their productions discussed in so clear and scientific a manner, and we feel sure that work of this kind will enable them in the end to dismiss many of their old "rule-of-thumb" methods as belonging to an age that has passed, and to place their manufactures upon a sound scientific footing, to the great advantage of both themselves and their customers. The book as heretofore is well illustrated and indexed.

The Chemistry of Paints and Painting. By A. H. Church, F.R.S., M.A., D.Sc., F.S.A., Professor of Chemistry in the Royal Academy of Arts, London. Third Edition, Revised and Enlarged. London: Seeley and Co., Lim., 38, Great Russell Street. 1901.

The third edition of Professor Church's book will be welcomed by painters and "picture makers" generally; the

plan of the earlier editions has not been altered, but many changes and additions have been made. In Chapter XXIV., on "The Study of Old Paintings and Drawings," a very interesting account is given of an examination of some of the valuable works in the National Gallery, furnishing adequate evidence of the instability of several favourite pigments largely used during the eighteenth and nineteenth centuries. Very many of the colours have failed, particularly the greens where verdigris was much in use.

As a result of recent experiments upon stability of pigments used in oil-painting, the colours more commonly used are classified in three degrees:—First, *permanent*; second, *liable to change*; and third, to be *definitely excluded from the palette*; this last includes the carmines, lakes, verdigris, indigo, and some few others. Accounts are given of the experiments of Professor Hartley, Professor Rood, Mr. Sampson, and Mr. Andrews, on water-colour pigments; also the report by Sir W. Abney and Dr. Russell to the Science and Art Department upon the same subject.

There is both a table of contents and a good index.

Introduction to the Study of Chemical Philosophy: The Principles of Theoretical and Systematic Chemistry. By William A. Tilden, D.Sc.Lond., Sc.D.Dub., F.R.S., Professor of Chemistry in the Royal College of Science, London. Tenth Edition. Completely Revised and Re-arranged, with Answers to Problems. London, New York, and Bombay: Longmans, Green, and Co., 39, Paternoster Row. 1901.

During the twenty-five years that have elapsed since the first edition of this work so many changes have taken place, so many fresh discoveries have been made and new theories propounded, that it has been found necessary to completely re-cast, and, in a large measure, to re-write this book, whilst retaining its general character.

A work of this kind by an author of such standing as Professor Tilden calls for little comment upon our part, but it is a great pleasure, amidst the multitude of books upon the teaching of chemistry that are brought to our notice, to find one that is not merely a *collection* of established principles and facts brought together for the benefit of the student, but rather the marshalling into intelligent order by a master mind of the fundamental principles and doctrines of the science, and their presentation to the student in such a manner as materially to assist him to "attain to the broad and philosophic views of chemistry as a whole." We only wish that there were more text-books of this stamp in circulation. The book comprises about 350 pages, exclusive of the "Answers to Problems," and is thoroughly indexed.

CORRESPONDENCE.

THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

Sir,—The Fellows of the Chemical Society, on being balloted last April, decided by a large majority that the day and hour of meeting of the Society could be altered with advantage to an earlier hour than 8 o'clock. The Council decided that the meetings should be held at 5.30 p.m. on Wednesdays, but this did not suit a number of the Fellows who were in the minority, and they held an extraordinary meeting, the result of which was that the Council altered the meetings for November and December of this session to Thursdays at 8 o'clock, and decided to hold the meetings in January, February, and March on Wednesdays at 5.30 p.m. Now I see that a section of the Fellows have got the President to summon an extraordinary meeting in order to pass a resolution to alter the meetings next January, February, and March to 8 o'clock on Thursdays.

Are the meetings of the Chemical Society held for the sole benefit of the London Fellows to the exclusion of those living at a distance from London, who, if the meetings were held at 5.30 p.m., could attend and return home the same night? This selfish and childish action of the minority is making the Society look ridiculous and undignified, and I hope all those Fellows living in London and in the country who can attend the meeting on December 12th, and who are in favour of the Society meeting at 5.30 p.m., will do so, and let the minority know that they are not going to rule the majority, and that they will demand a ballot of the whole of the Fellows.

I would suggest as a compromise that the meetings be held on Thursdays at 5.30 and 8 o'clock alternately.

The proposed modification of By-law XI. is an insult to those gentlemen who give their time to govern the Society, and practically a vote of no confidence in them.

Hoping that you will insert this letter in this week's issue of the Chemical News, I enclose my card.—I am, &c.,

A Fellow of the Chemical Society.

November 30, 1901.

A NEEDED REFORM IN CHEMICAL NOMENCLATURE.

To the Editor of the Chemical News.

Sir,—When chemistry adopted its modern system of nomenclature, when it tried to tell the composition of a substance instead of the name of the man who discovered it, a decided advance was made. Now another step should be taken in the same direction. Chemical laws as well as chemical substances should be appropriately named. An experience of several years has shown me how much unnecessary labour is put upon a student when he is compelled to learn what "Avogadro's" hypothesis is, or "Dalton's" theory, or "Gay-Lussac's" law, or any one of a number of others; while he could learn all these with little difficulty if they possessed descriptive names. There is a tendency in the right direction at the present time, and some of the more modern writers very properly give the law and not the discoverer the prominence; but there are still too many who lay undue stress on the old names.

It may be objected by some that the use of the discoverer's name is the only method we have of showing our respect for him; but even those who would urge such a thing would not advocate the use of "Glauber's" salt, or of any of the old names of chemical compounds merely for the purpose of perpetuating the memories of the pioneers of chemistry.

I have been impelled to call attention to this need by noticing that while some of the recent text-books adopt the more rational method, too many still adhere to the clumsy old way. It certainly would be a move in the direction of simplicity if chemical writers would agree to re-name some of the old laws and theories so that the names would correspond with others used in the science. —I am, &c.,

Edward Booth.

University of California, Berkeley.
November 10, 1901.

MANGANESE IN WATER.

To the Editor of the Chemical News.

Sir,—The letter from Mr. T. H. Byron in the Chemical News, vol. lxxxiv., p. 183, calls to my mind an analysis of water recently made by me. This water was from a spring whose healing virtues were in high repute among the people of the locality. It was supposed to be efficacious for all ills, from consumption to mange. As a matter of fact it does seem to possess considerable

therapeutic value. Analysis showed it to be a weakly alkaline carbonated water. The only unusual ingredient was manganese, which was present to the amount of 2 parts per million, calculated as MnO. The sediment from the water on standing consisted chiefly of iron hydroxide with a little manganese. As the manganese did not deposit to any appreciable extent on standing or boiling, it could hardly have been present as a bicarbonate, though it would naturally be calculated as such.

The result of this analysis led me to look up the subject of manganese in mineral waters, and I have found it reported in nearly seventy analyses of American waters, in nearly half of these, however, only as "trace." In one water 41 parts per million of manganese sulphate was given, and in three other cases over 20 parts, as sulphate, bicarbonate, and carbonate respectively. In numerous instances several of the analyses were by the same chemist, and I think it may be inferred that manganese is often present, but not estimated or looked for.

In Dr. Crook's recent work, "The Mineral Waters of the United States and their Therapeutic Uses," manganese is omitted from the list of ingredients of mineral waters, but is later mentioned briefly in the description of the components. Here it is alluded to as having been detected in a few springs, and it is added that "it is probably a useful auxiliary to iron in several springs, but its claims are not such as to entitle it to an important place in therapeutics."

Of late years some attention has been given to the value of manganese in therapeutics, but it still needs much investigation, and it is by no means impossible that the manganese present in some mineral waters may possess a real value.—I am, &c.,

JAS. LEWIS HOWE.

Washington and Lee University,
Lexington, Virginia, November 16, 1901.

NOMENCLATURE OF THE IONS.

To the Editor of the Chemical News.

SIR,—The paper by Dr. Walker printed in a recent issue of the CHEMICAL NEWS (vol. lxxxiv., p. 162), and dealing with the nomenclature of ionic chemistry, was exceedingly timely, and disposed admirably of most of the difficulties. There is one other term, however, the need of which will be felt by any one endeavouring to discuss the subject before his classes. A word is needed to express *materials which are capable of undergoing ionisation.*

The use of the term salt for such substances leads to confusion. It has indeed been pointed out that acids are simply salts of hydrogen and bases salts of hydroxyl. But in ordinary language we still require an expression for salt-like compounds which are neither acids nor bases, and the use of the term salt in this sense is so firmly established that it seems better to leave its significance unchanged. For materials which are salts in the wider sense, that is bodies which undergo ionisation, I have found the word *ionogen* very useful. The word electrolyte seems to be applied rather to the solution as a whole than to the substance dissolved. In any case it has the unfortunate property of conveying to the beginner the impression that it is a liquid in which ions are produced by the electric current, and are not present until the current is used.—I am, &c.,

ALEXANDER SMITH.

The University of Chicago,
November 14, 1901.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 2nd inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair. Sir Thomas Barlow, Bart., M.D., Mr. K. M. Chance, Sir Walter G. F. Phillimore, Bart., D.C.L., and The Hon. C. S. Rolls were elected Members. The special thanks of the Members were returned to Dr. Ludwig Mond, F.R.S., for a donation to the Fund for Experimental Research.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Seances, de l'Académie des Sciences. Vol. cxxxiii., No. 20, November 11, 1901.

A New Method of Manipulation of Gases Liquefied in Sealed Tubes.—Henri Moissan.—The use of liquefied gases is becoming so common that the author makes a series of experiments on the precautions necessary for their preservation. During his experiments with Professor Dewar at the Royal Institution, fluorine was kept in a liquid state at a temperature of −80°, produced by the slow evaporation of a mixture of solid carbonic acid in ethyl alcohol. Careful experiments on this mixture show that a constant temperature of −85° can be produced by its slow evaporation. Solid carbonic acid and methyl chloride give a lower temperature (−90°), acetic ether saturated with solid carbonic acid gives −95°, and, finally, acetone, which dissolves a great quantity of the anhydride, goes down to −98°. A still lower temperature (−110°) may be obtained by cooling dry air by the rapid evaporation of the last freezing mixture. A still further reduction in temperature (−182·5°) is produced by the use of liquid air, or better liquid oxygen. When it is necessary to find the action of a liquefied gas on a solid, the pressure furnished at ordinary temperatures (if the critical point is high enough to maintain the liquid in the sealed gas tube) may be utilised. In order to seal the tube the liquid must be reduced to a solid state. Such tubes should be capable of sustaining a pressure of 200 to 300 atmospheres. The author uses crystal tubes 10 m.m. external and 6 m.m. internal diameter. In such tubes ammonia, chlorine, and sulphuretted hydrogen were preserved in the liquid state for years. The author finally mentions that all these manipulations are dangerous, and it is necessary to take the greatest care in handling glass tubes containing gases and liquids under these enormous pressures.

Action of Ammonium Metal on Sulphuretted Hydrogen.—Henri Moissan.—At a temperature somewhere between −75° and −70° the author allows liquid sulphuretted hydrogen to react on lithium-ammonium, giving lithium sulphide, ammonia, and free hydrogen. The molecule $(NH_4)_n$, if it is produced in this reaction, has no stability at this low temperature, and it decomposes into ammonia and hydrogen. He next allows liquid sulphuretted hydrogen to act on calcium-ammonium at the temperature of boiling sulphuretted hydrogen (−73°), when the same decomposition takes place. Calcium sulphide is formed and hydrogen evolved. From the weight of calcium before the experiment (0·0476 grm.) and the volume of hydrogen collected (25·87 c.c.) the reaction is apparently represented by the equation—

$$(NH_4)_4Ca.2NH_3 + H_2S = CaS + 6NH_3 + H_2.$$

The theoretical quantity of hydrogen for the weight of calcium taken is 26·7 c.c. It was impossible to conduct these experiments at a lower temperature, the ammonia becoming solid at −75°. Ammonium, therefore, which hitherto has been only represented by a theoretical conception, apparently does not exist at the temperature of −73° in presence of liquid sulphuretted hydrogen.

Formation of Ozone.—A. Chassy.—When an electric current is passed through oxygen, ozone is formed in relatively small quantity. The proportion of ozone increases at first rapidly, but then tends towards a certain limit, as in the phenomena of dissociation. The author examines the manner in which the increase of ozone takes place in a definite mass of oxygen and having a perfectly constant current. The first important point which he establishes is that the law of the increase of ozone is the same whatever the intensity of the electric current. His

numerical measurements are given in the form of a table. The curve on which these numbers lie is asymptotic, the quantity of ozone tending towards a limit, which only depends on the temperature, and not on the intensity of the current, but which is difficult to determine with precision.

MISCELLANEOUS.

Royal Institution.—The following are the Lecture Arrangements at the Royal Institution, before Easter:—

Professor J. A. Fleming, Six Lectures (adapted to young people) on "Waves and Ripples in Water, Air, and Æther."

Dr. A. Macfadyen, Six Lectures on "The Cell: its Means of Offence and Defence. Immunity."

Mr. W. N. Shaw, Two Lectures on "The Temperature of the Atmosphere; its Changes and their Causes."

Professor E. B. Poulton, Two Lectures on "Recent Researches on Protective Resemblances, Warning Colours, and Mimicry in Insects."

Dr. A. S. Murray, Three Lectures on "Recent Excavations at Delphi and in the Greek Islands."

The Rev. John Watson (Ian Maclaren), Three Lectures on "The Scot of the 18th Century: 1—At Home, 2—In Kirk, 3—With his Books."

Sir Henry Craik, Two Lectures on "Scotland's Contribution to the Empire."

Two Lectures on "Caricature in and out of Parliament," by Mr. E. T. Reed.

Four Lectures on "The Landmarks in the History of Opera: Gluck, Mozart, Weber, Wagner," by Mr. W. H. Hadow."

Six Lectures on "Some Electrical Developments," by Lord Rayleigh.

The Friday Evening Meetings will commence on January 19th, when Lord Rayleigh will deliver a Discourse on "The Interference of Sound." His Grace the President will, after the Discourse, unveil and present to the Institution, on behalf of the Subscribers, a Bust by Mr. Onslow Ford, R.A., of Sir Frederick Bramwell, Bart., Honorary Secretary of the Royal Institution from 1885 to 1900. Succeeding Friday Evening Discourses will be delivered by Mr. H. G. Wells, Professor A. Crum Brown, Professor Arthur Gamgee, Major P. A. MacMahon, Mr. W. Duddell, Professor Henry A. Miers, Professor H. Becquerel, Professor E. Ray Lankester, Geheimrath Professor Otto N. Witt, and other gentlemen.

The Energy of some Metallic Hydrates, Deduced from the Hydrolysis of the Salts.—G. Carrara and G. B. Vespignani. — The authors have measured this hydrolysis by means of the electric conductivity, on the one hand, and by means of the catalysis of acetate of methyl and the inversion of sugar, on the other hand. The conclusions to be drawn from the tables of the results are:—1. The basic energy of the metallic hydrates is in accordance with the position these elements occupy in the periodic system; this energy diminishes in the order, Mg—Cu—Zn—Cd—Al.Fe. 2. Hydrate of alumina is a more energetic base than ferric hydrate. 3. The basic ferric chloride is always much more hydrolysed than the sulphate, and this latter more than the basic sulphate of alumina. 4. Even in the presence of a considerable excess of potash, hydrated alumina only gives monopotassic aluminate. The di- and tripotassic aluminates are, at the dilutions at which the experiments were carried out, from $\frac{1}{2}$ to $\frac{2}{3}$ hydrolysed. 5. Hydrate of alumina is more basic than acid. Sulphate of alumina is hydrolysed fourteen times less than the aluminate. 6. The oxides of lead and zinc, dissolved in an excess of potash at the dilution $v=5$, form monopotassic plumbite and dipotassic zincate.—*Gazz. Chim. Ital.*, [2], vol. xxx., p. 35.

Contribution to our Knowledge of Indican.—H. Ter Meulen.—The indican used by the author was prepared from the leaves of the *Polygonum tinctorium* and the *Indigofera leptostachya*. These leaves, after immersion in boiling water for a few minutes, were systematically exhausted by warm water (2½ parts of water to 1 part of leaves); the liquid was filtered after precipitation by hot baryta water, and the separation of the excess of baryta by means of CO_2; it was then evaporated to dryness under reduced pressure; the residue was taken up with methylic alcohol, and the solution thus obtained treated with double its volume of ether, which precipitates various impurities. The ethero-methylic solution, when distilled, leaves a residue which, when taken up by water, gives crystalline indican in the form of small lance-like crystals, probably belonging to the orthorhombic system. Indican crystallises with $3H_2O$, and fuses at 51°; when anhydrous it fuses at 100—102°; it is soluble in water, acetone, and methylic and ethylic alcohols, slightly soluble in C_6H_6, $CHCl_3$, CS_2, &c. It is levogyre (deviation about 2° for a 2 per cent solution, $l=200$ m.m.). If the solution be heated with hydrochloric acid and the indoxyl be eliminated by oxidation, the rotatory power becomes right-handed; the sugar formed by the hydrolysis of indican has not been characterised. Analyses and cryoscopic determinations enable us to confirm the formula given by Marchlewski for anhydrous indican, viz., $C_{14}H_{17}NO_6$, who considers it to be a glucoside, splitting up into glucose (1 molecule), and indoxyl (1 molecule). —*Revue. Trav. Chim. P.-B.*, vol. xix., p. 166.

MEETINGS FOR THE WEEK.

Monday, 9th.—Society of Arts, 8. (Cantor Lectures). The Chemistry of Confectioners' Materials and Processes," by W. Jago, F.C.S., F.I.C.

Wednesday, 11th.—Society of Arts, 8. "Aluminium," by Prof. Ernest Wilson, M.Inst.E.E.

Friday, 13th.—Physical, 5. "On Circular Filaments and Circular Magnetic Shells Equivalent to Circular Coils, and on the Equivalent Radius of a Coil," by Prof. Thomas R. Lyle. "Air Pressures used in Playing Brass Instruments," by Dr. Barton and S. C. Laws. "A New Hygrometric Method," by E. B. H. Wade.

ST. THOMAS'S HOSPITAL MEDICAL SCHOOL.

JUNIOR DEMONSTRATOR OF CHEMISTRY AND PHYSICS.

The General Committee will shortly proceed to make this Appointment.

The Demonstrator will be required to devote his whole time to the teaching of Chemistry and Physics, under the direction of the Lecturer in Chemistry. Opportunity for Research Work will be afforded.

The stipend is £80 per annum and fees.

Applications, with testimonials, should be sent to the Medical Secretary, St. Thomas's Hospital, S.E., not later than December 10.

H. G. TURNEY, M.A., M.D.(Oxon.), Dean.

Chemist (Ph.D., Vienna), wants fresh Appointment in Chemical Works or Laboratory. Experienced in Organic and Inorganic Chemistry; special knowledge and experience in Metallurgy. Small salary accepted until abilities proved.—Address, Dr. F. O., Chemical News Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

Public Analyst has a Vacancy for a Pupil Assistant without Salary.—Address, B. F. H., Chemical News Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

RESEARCH CHEMIST.—Wanted for a Works in South of England, thoroughly trained Chemist, good at Research, Inorganic and Physical.—Address, with full particulars and terms, to "W. L.," care of J. W. Vickers, 5, Nicholas Lane, E.C. None but those with highest qualifications need apply.

GOVERNMENT GRANT to defray the expenses of Scientific Investigations. Applications for the year 1902 must be received at the Offices of the ROYAL SOCIETY not later than January 31st next, and must be made upon printed forms to be obtained from the CLERK TO THE GOVERNMENT GRANT COMMITTEE, Royal Society, Burlington House, London, W.

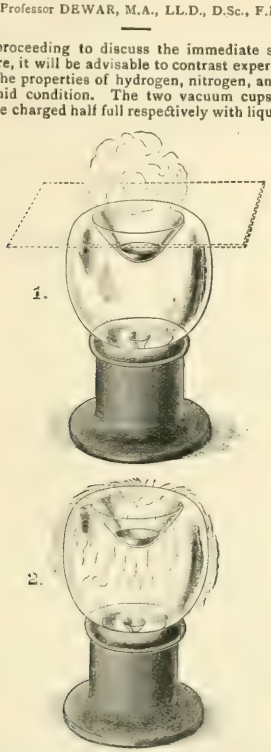
THE CHEMICAL NEWS.

Vol. LXXXIV., No. 2194.

SOLID HYDROGEN.*

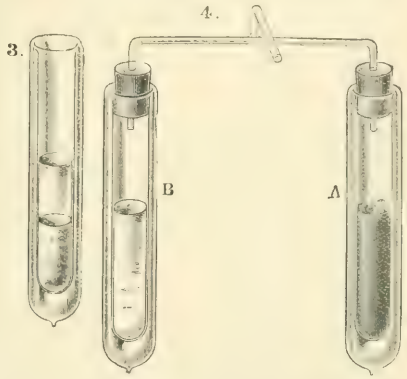
By Professor DEWAR, M.A., LL.D., D.Sc., F.R.S.

Before proceeding to discuss the immediate subject of this lecture, it will be advisable to contrast experimentally some of the properties of hydrogen, nitrogen, and oxygen in the liquid condition. The two vacuum cups (Figs. 1 and 2), are charged half full respectively with liquid hydro-



gen and liquid air. When the cup containing the liquid air is placed in front of the electric lamp, the image thrown on the screen reveals the continual overflow of a dense vapour round the outer walls of the vessel. The saturated vapour coming from the steady ebullition of liquid air is three times denser than the free air of the room, and the result is it falls through that air just as if it were a dense gas like carbonic acid or ether vapour. To observe this phenomenon, the vacuum cup must be shallow, otherwise the vapour gets heated up before reaching the mouth of the vessel, and no difference of density in the air coming off is observed. We will now project the image of the cup containing liquid hydrogen, covered loosely in this case with a glass plate, upon the screen; here, no heavy vapour escaping round the sides is visible. The vapour of the boiling liquid hydrogen has a density nearly equal to the air of the room, but as it gets very rapidly heated up by the glass cover the gas that is escaping is seen to rise in air like any light gas. On now removing the glass plate, a very different phenomenon is observed, which contrasts markedly with the behaviour of the liquid air in the former vessel. The cup and the air above is filled with a dense surging snowstorm of solid air; the air coming in contact with the excessively cold hydrogen vapour is suddenly solidified, and a part of it falls into the liquid hydrogen, causing more rapid evaporation, thereby intensifying the cloud condensation. After the mist has disappeared and all the liquid hydrogen gone, the cup contains a white deposit of solid air. This shortly melts, and on allowing the nitrogen to boil off, the presence of oxygen can be shown by the ignition of a red-hot splinter of wood. Such effects are easily understood when we remember that the boiling-point of hydrogen is proportionally as much below the boiling-point of air as the latter is below the ordinary temperature of this room.

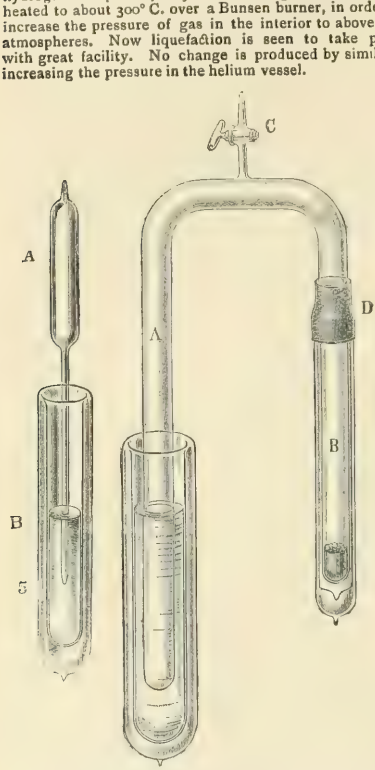
In order to observe the individual behaviour of the constituents of the air at temperatures below their ordinary boiling-points it is advantageous to place liquid nitrogen and oxygen in separate vacuum vessels, so connected that they may be simultaneously exhausted, as is represented in Fig. 4. On starting the air-pump both liquids enter



into rapid ebullition. As the exhaustion gets higher the temperature of each liquid gets lower and lower, and if the melting point is finally reached in either liquid it must shortly begin to solidify. This condition is quickly brought about in the case of the vessel A containing the liquid nitrogen, which passes rapidly into the condition of a dense white snow; but no amount of time spent in maintaining a good exhaustion (5 to 10 m.m. pressure) has any effect in changing the liquid condition of the oxygen in B. Oxygen, in fact, remains liquid at temperatures where nitrogen is solid. The snow of solid air produced by the evaporation of liquid hydrogen in the previous experiment, might thus be made up of solid nitrogen and a liquid rain of oxygen. To show that the temperature of boiling hydrogen solidifies oxygen, some of the latter liquid is placed in a vacuum test-tube O (Fig. 3), and liquid hydrogen H is poured on its surface, when the liquid oxygen is quickly transformed into a clear blue solid ice. Both oxygen and nitrogen, and we shall see later, hydrogen, can be changed into the condition of transparent ice as well as into the snowy state. A closed vessel filled with any gas at atmospheric pressure, of such a form that a portion of the surface in the shape of a narrow quill tube can be cooled in boiling liquid hydrogen like B, Fig. 5, shows condensation of the gas to the solid state; the only exceptions being helium and hydrogen itself. Here are two vessels of the

* A Discourse delivered before the Royal Institution, April 6, 1900.

same shape as A, B, Fig. 5. The first contains helium showing no condensation when the part B is cooled; the second is filled with hydrogen, which equally shows no change of state under the conditions of the experiment. It is easy, however, to make the hydrogen vessel show liquefaction. For this purpose the experiment with the hydrogen is repeated, only before doing so the part A is heated to about 300° C. over a Bunsen burner, in order to increase the pressure of gas in the interior to above two atmospheres. Now liquefaction is seen to take place with great facility. No change is produced by similarly increasing the pressure in the helium vessel.



The extraordinary command liquid hydrogen gives us over the transition of state in matter may be best illustrated by the use of a new kind of cryophorus. Wollaston's celebrated instrument operates by forcing the evaporation of water in a closed vessel by condensing its vapour in a part of the receiver at a distance from the fluid, thereby causing a lowering of temperature in the latter until freezing takes place. Hence the name cryophorus or cold-bearer. Instead of using water we may now show that the same principle may be applied to the solidification of nitrogen at a distance, instead of water. The sole difference in this case is that the liquid nitrogen must be isolated from the influx of heat by being placed in a vacuum vessel and the condensation of its vapour must be effected by the use of liquid hydrogen.

No boiling-out operation is necessary with the cryophorus we are about to use. The apparatus is shown in Fig. 6. The vacuum tube B contains liquid nitrogen. It is fitted on by an indiarubber joint to a wide piece of glass tubing doubly bent at right angles, A D; and in order to allow the gas from the boiling liquid to escape before the experiment begins, an aperture C is left which can be closed with a stopcock. On closing C, and inserting a part of the tube A into a vessel containing liquid hydrogen, the gas within is condensed, and thereby the pressure of the vapour in the interior of the vessel is reduced, forcing the liquid nitrogen in the other part of the apparatus to boil with great violence. In a few minutes the temperature of the nitrogen is so much reduced that it passes into the solid state. Many other liquid gases might be used to replace the nitrogen in this experiment. In making a selection, however, it is necessary to take only those bodies that possess a reasonably high tension of vapour at the melting point. The process would not succeed easily with a substance like oxygen, that has no measurable tension of vapour in the solid condition.

In the autumn of 1898, after the production of liquid hydrogen was possible on a small scale, its solidification was attempted by boiling under reduced pressure. At this time, to make the isolation of the hydrogen as effective as possible, the liquid was placed in a small vacuum test-tube, placed in a larger vessel of the same kind. Excess of hydrogen partly filled the annular space between the two vacuum vessels. On diminishing the pressure by exhaustion the evaporation was mainly thrown on the liquid hydrogen in the annular space between the tubes. In this arrangement the outside surface of the smaller tube was kept at the same temperature as the inside, so that the liquid hydrogen for the time was effectually guarded from influx of heat. With such a combination the liquid hydrogen was evaporated under diminished pressure, yet no solidification took place. Seeing experiments of this kind required a large supply of the liquid, other problems were attacked, and further attempts in this direction of producing the solid for the time abandoned. During the course of the present year many varieties of electric resistance thermometers have been under observation, and with some of these the reduction of temperature brought about by exhaustion was investigated. Thermometers constructed of platinum and platinum-rhodium (alloy) were only lowered 1½° C. by exhaustion of the liquid hydrogen, and they all gave a boiling-point of −245° C., whereas the reduction in temperature by evaporation *in vacuo* ought to be 5° C., and the true boiling-point from −252° C. to −253° C. In the course of these experiments it was noted that almost invariably a slight leak of air occurred which became apparent by its being frozen into an air-snow in the interior of the vessel, where it met the cold vapour of hydrogen. When conducting wires covered with silk have to pass through indiarubber corks it is very difficult at these excessively low temperatures to prevent leaks, when corks get as hard as a stone, and cements crack in all directions. The effect of this slight air leak on the liquid hydrogen when the pressure got reduced below 60 m.m., was very remarkable, as it suddenly solidified into a white froth-like mass like frozen foam. My first notion was that this body might be a sponge of solid air containing liquid hydrogen. The ordinary solid air obtained by evaporation *in vacuo* is a magma of solid nitrogen containing liquid oxygen. The fact, however, that this white solid froth evaporated completely at the low pressure without leaving any substantial amount of solid air, led to the conclusion that the body after all must be solid hydrogen. This surmise was confirmed by observing that if the pressure, and therefore the temperature, of the hydrogen was allowed to rise, the solid melted when the pressure reached about 55 m.m. The failure of the early experiment must then have been due to supercooling of the liquid, which presumably is prevented by contact with metallic wires and traces of solid air. On the other hand, it is possible the pressure under which the ebullition took place might never have been low enough to reach the solid state.

(To be continued).

ANALYSIS OF A SILURIAN LIMESTONE ROCK.

By Dr. T. L. PHIPSON.

THIS is one of the most ancient of stratified rocks; it is called in Herefordshire, whence my specimens were taken, by the name of "bastard limestone." On account of its large admixture with "old red" sandstone, it is not considered fit to produce lime for mortar. It forms a portion of the strata known to geologists as "lower Ludlow rock." The compact stone is brownish red, variegated with pale green and white, and passes into a schistous rock of a greenish grey colour containing as much as 60 per cent of sandstone. It yields a pink powder.

The specific gravity of the compact crystalline stone varies from 2·75 to 3·01. It is rather fragile, but is employed on the farms for building purposes, &c. It contains a very large number of elements; the sandstone contains about 1 per cent of black titanic sand of a greater specific gravity. The analysis of the more compact portion of this rock has given me the accompanying figures.

Water, with some hydrocarbon gas	1·20—1·60	
Peroxide of iron	3·76	
Alumina	0·78	
Oxide of zinc	0·23	As silicate.
„ manganese	1·70	
„ nickel	trace	
Ceric oxide and rare earths	0·08	Separated as oxalates.
Titanic acid	0·12	As black titanic iron in the sandstone.
Vanadic acid	0·10	
Phosphoric acid	0·20	
Soluble silica	0·41	
Lime	30·69	
Magnesia	0·47	
Alkalis	0·03	
Tellurium	0·01	Probably as telluride of lead.
Gold	faint traces	
Lead	0·03	Found, oxide of lead 0·04.
Sulphuric acid	trace	
Chlorine	trace	
Quartz sand	34·00—32	(in compact stone) to 60 (in schistous rock).
Baryta	trace	
Carbonic acid (by difference)	26·19	Found, 25·96.
	100·00	

The samples of this stone were taken about 2 feet from the surface in a quarry at Little Dewchurch, Herefordshire; it contains, dispersed throughout it, very minute tin-white specks which might be taken for mica, but which appear to be tellurium or telluride of lead.

THE QUANTITATIVE SEPARATION AND DETERMINATION OF URANIUM.*

By EDWARD F. KERN.

(Concluded from p. 273).

PART III.—ESTIMATION OF URANIUM IN PITCHBLENDE.

IN order to apply the preceding separations and determinations, to an actual technical assay of pitchblende, samples of the ore were analysed by two entirely different methods; the Patera method with modifications, and the "ether extraction" method. In both cases the uranium was determined in several different ways. These assays gave an actual comparison of results, and at the same time tested the separations and estimations of uranium which were worked out on pure solutions.

The assays were first made by Patera's method as follows:—Eight samples of the finely divided ore (about 1·3 grms) were weighed into small beakers, and decomposed by adding 5 c.c. water and 10 c.c. nitric acid (sp. gr. 1·42).

Complete solution was brought about by heating almost to boiling in covered beakers on a hot asbestos plate till the residues were almost white in colour, then the watch-glasses were removed, and the solutions slowly evaporated to a pasty mass. After cooling, the masses were taken up with 50 c.c. water and 3 c.c. nitric acid (sp. gr. 1·42), and the solution brought to boiling. The silica was filtered off and washed with boiling water, and rejected. The filtrates were diluted to 200 c.c. volume, and hydrogen sulphide gas passed through the cold solutions for one hour. The precipitates of sulphides of lead, copper, &c., were filtered, washed with hydrogen sulphide water, and rejected. The filtrates from the sulphides were at first slowly heated, and finally boiled in order to expel hydrogen sulphide gas and to oxidise the iron. Evaporation was continued till the bulk of the solutions was about 125 c.c., then the separated sulphur was filtered off and washed. The solutions were brought to boiling, and 150 c.c. of a saturated solution of sodium carbonate added, boiling was continued for twenty minutes, after which the precipitates (principally ferric hydroxide) were filtered off, and washed three times by decantation and four times on the filter with hot water. The filtrates containing the uranium were evaporated to half volume (about 150 c.c.), slowly neutralised with hydrochloric acid (sp. gr. 1·20), and about 3 c.c. in excess, then boiled for half-an-hour till all carbon dioxide was expelled. The uranium was precipitated from the hot solutions by means of a slight excess of sodium hydroxide (free from carbonate), and boiling for about ten minutes, keeping the beakers covered with watch-glasses. The orange-yellow precipitates of sodium uranate were allowed to settle, the supernatant liquids poured through filters, and the precipitates twice washed by decantation, and three times on the filters with hot water.

Precipitates Nos. 1 and 2 were dried in a hot oven, separated from the filters and ignited in platinum crucibles, after which the ash of the papers was added to the crucibles, and ignition continued at "redness" for five minutes. The residues on cooling were treated several times with hot water, after each treatment pouring the water through a small filter. The filters were dried, ignited, added to the crucibles, and re-ignited at "redness"

* Contribution from the Havemeyer Laboratories of Columbia University. From the *Journal of the American Chemical Society*, xxiii., No. 10.

for ten minutes. After cooling in a desiccator, they were weighed. According to Patera, the residue consists of $NaO.2(U_2O_3)$, 100 parts of which contain 88·3 parts of U_3O_8.

Precipitates Nos. 3, 4, 5, 6, and 7 were dissolved from the filters by warm dilute hydrochloric acid (sp. gr. 1·13), and caught in small beakers. The solutions were evaporated twice to dryness on a warm asbestos plate, the second time with 10 c.c. hydrochloric acid (sp. gr. 1·20). The dry residues were taken up with 3 c.c. hydrochloric acid, diluted to 100 c.c., and brought to boiling. The silica, dissolved from the beakers by the strong alkali solution, was filtered off, and washed with boiling water.

Solutions Nos. 3 and 4 were brought to boiling, 5 c.c. hydrochloric acid (sp. gr. 1·20) added, and ammonia (sp. gr 0·90) in excess. The solutions were boiled for fifteen minutes, thus changing the voluminous amorphous precipitate of yellow ammonium uranate into a more crystalline form, darker in colour, which was readily and rapidly washed. The precipitates were allowed to settle, the supernatant liquids poured through filters, and the precipitates washed three times by decantation, and twice on the filter with a hot dilute solution of ammonium chloride (2 grms. of salt to 100 c.c. water). The precipitates were dried, placed in platinum crucibles together with filter-paper, and slowly ignited till the paper was completely destroyed, then ignited in a blast-flame for ten minutes, after which they were slowly cooled in a gradually decreasing Bunsen flame. During ignition the crucibles were placed in a slanting position in order to allow of free circulation of air in the crucible, thus obtaining complete oxidation to U_3O_8. They were allowed to cool in a desiccator and weighed.

Solution No. 5 was diluted to 150 c.c., brought to boiling, and 5 c.c. hydrochloric acid (sp. gr. 1·20) added. The solution was neutralised with ammonia (sp. gr. 0·90) and 5 c.c. added in excess. Acetic acid was slowly added to the hot solution, stirring all the while, till the yellow precipitate disappeared. The uranium was then precipitated by means of ammonium dihydrogen phosphate, adding about twice as much as was necessary for complete precipitation. The solution was boiled for fifteen minutes, allowed to cool, then filtered, and the precipitate washed four times on the filter with a hot 2 per cent solution of ammonium chloride. The precipitate was dried, separated from the filter-paper which was first ignited in a porcelain crucible, after which the precipitate was added and ignited at low redness for ten minutes over a Bunsen flame. The crucible was allowed to cool, the residue moistened with a few drops of nitric acid (sp. gr. 1·42), dried on a hot plate, and re-ignited at low redness for ten minutes. The lemon-yellow coloured precipitate of uranyl pyrophosphate, $(UO_2)_2P_2O_7$, was weighed, and the U_3O_8 equivalent obtained by multiplying the weight by 0·66815.

Solutions Nos. 6 and 7 were evaporated to about 30 c.c. volume, allowed to cool, 30 c.c. sulphuric acid (sp. gr. 1·84) added, and evaporation continued to dense white fumes. The solutions were poured into 250 c.c. Erlenmeyer flasks, diluted to 150 c.c., and reduced at boiling temperature by about 50 grms. of pure granulated zinc. The reductions were continued for one and a-half hours till the solutions were a clear green colour. The solutions were then poured into a large Erlenmeyer flask, which contained about 1 grm. of dry sodium carbonate, diluted to 500 c.c., and titrated by 0·01 normal potassium permanganate solution.

Precipitate No. 8, of sodium uranate, was dissolved from the filter with warm dilute nitric acid (1 part acid, sp. gr. 1·42, and 2 parts water), and caught in a small beaker. The solution was evaporated to dryness twice, the second time with 10 c.c. nitric acid (sp. gr. 1·42). The dry mass was taken up with 5 c.c. of 50 per cent acetic acid, diluted to 50 c.c., and the solution boiled till all salts were dissolved. The silica, which was dissolved from the beaker by the strong sodium carbonate solution, was filtered off, and washed with hot water. The solution was diluted to exactly 100 c.c. in a graduated flask, 50 c.c. were measured into a large clean platinum dish, and the uranium determined by electrolysis as follows:—Added 0·5 grm. sodium acetate, diluted to 125 c.c., and electrolysed at a temperature of 65° to 75° C., with a current of $N.D._{100}=0·8$ to 1·0 ampère. The uranium was completely precipitated, as hydrated protosesquioxide, within eight hours. The electrolyte was emptied into a beaker, and the black deposit washed with warm water. The electrolyte and the washings were poured through a fluted filter-paper, the paper several times rinsed with hot water, dried and ignited on the cover of a platinum crucible, and the ash added to the dish. The dish was then dried, ignited over a blast-lamp for ten minutes, and allowed to cool in a gradually decreasing Bunsen flame. It was placed in a desiccator, and, after thoroughly cooling, was weighed. The ignited deposit consisted of U_3O_8.

The results obtained by this series of assays are shown in Table VIII. (Experiments 1 to 13).

Estimation of Uranium in Pitchblende by the Ether Extraction Method.—The ether extraction method differs from the Patera method in that the uranium is not separated from the fourth group members by means of sodium carbonate, but by ether and by ammonium carbonate. The iron was separated from uranium and the other metals by shaking the hydrochloric acid solution with ether, free from alcohol. The uranium was then separated from the other associated metals (aluminum, manganese, zinc, and nickel) by means of ammonium carbonate.

The procedure was as follows:—Seven samples (about 1·3 grms.) of the finely divided pitchblende were decomposed with boiling dilute nitric acid (1 part acid, sp. gr. 1·42, and 1 part water) till the residues which remained were almost white in colour. The solutions were then evaporated to a pasty mass, taken up with 15 c.c. hydrochloric acid (sp. gr. 1·20), and evaporated to dryness twice, the second time with 10 c.c. hydrochloric acid (sp. gr. 1·20). The salts were taken up with 5 c.c. hydrochloric acid (sp. gr. 1·20), diluted to 150 c.c., brought to boiling, and the silica filtered off and washed. The filtrates were diluted to 250 c.c., and the lead, copper, &c., precipitated as sulphides by passing hydrogen sulphide gas through the cold solutions for about an hour. The filtrates from the sulphides were evaporated slowly to about 150 c.c., and boiled for a few minutes in order to expel all hydrogen sulphide. The separated sulphur was filtered off and washed. The solutions were brought to boiling, 5 c.c. nitric acid (sp. gr. 1·42) added, and boiling continued till the iron was completely oxidised, after which ammonia (sp. gr. 0·90) was added in excess, and boiling continued for fifteen minutes. The precipitates of impure ferric hydroxide, ammonium uranate, &c., were filtered off, and washed with a warm 2 per cent solution of ammonium chloride. The wet precipitates were dissolved from the filters with warm dilute hydrochloric acid (sp. gr. 1·10), and caught in small beakers. The solutions were twice evaporated to dryness, the second time with 10 c.c. hydrochloric acid (sp. gr. 1·20). The dry salts were taken up with with 15 c.c. hydrochloric acid (sp. gr. 1·10), the beakers covered with watch-glasses, and the solutions heated till all salts had dissolved, but not long enough to lose any of the acid by evaporation. After cooling, the solutions were emptied into 250 c.c. separatory funnels, and the beakers rinsed out four times with 5 c.c. hydrochloric acid (sp. gr. 1·10). Fifty c.c. of pure ether which had previously been shaken up with hydrochloric acid (sp. gr. 1·10), were added to each funnel, and thoroughly shaken for about seven minutes with the aqueous hydrochloric acid solutions, occasionally relieving the pressure, due to evaporation of ether. After agitation, the funnels were allowed to stand for a few minutes till the two solutions separated, then the lower aqueous layers were run into other separatory

TABLE VIII.

Experiment. No.	Amount of ore taken. Grms.	Weighed as—	Weight. Grm.	Calculated to U_3O_8 equivalent.	Per cent of U_3O_8.	Average. Per cent.
1.	1·2863	$NaO(U_2O_3)_2$	0·3064	0·27055	21·03	20·76
2.	1·3278	$NaO(U_2O_3)_2$	0·3071	0·27117	20·49	
3.	1·2882	U_3O_8	0·2616	0·26160	20·31	20·46
4.	1·2880	U_3O_8	0·2653	0·26530	20·60	
5.	1·2840	$(UO_2)_2P_2O_7$	0·3297	0·25940	20·20	20·20
6.	1·4004	Titrated	—	0·29090	20·77	20·63
7.	1·2164	Titrated	—	0·24940	20·50	
8.	0·6416	U_3O_8	0·1306	0·13060	20·36	20·36
9.	1·2405	U_3O_8	0·2565	0·2565	20·67	20·61
10.	1·2409	U_3O_8	0·2550	0·2550	20·55	
11.	1·2390	$(UO_2)_2P_2O_7$	0·3233	0·2545	20·54	20·66
12.	1·2991	$(UO_2)_2P_2O_7$	0·3431	0·2701	20·79	
13.	2·2892	Titration	—	0·2672	20·80	20·71
14.	1·2828	Titration	—	0·2646	20·63	
15.	0·6207	U_3O_8	0·1283	0·1283	20·67	20·67

funnels. The ether layers containing most of the iron, were twice shaken up with 5 c.c. hydrochloric acid (sp. gr. 1·10), and the washings added to the main solutions containing the uranium. The second extractions were made with 50 c.c. ether, and the third with 30 c.c. ether. In both cases the ether solutions were twice washed with 5 c.c. hydrochloric acid (sp. gr. 1·10). The aqueous hydrochloric acid solutions, now free from iron, contained a small amount of ether, which was allowed to evaporate spontaneously by exposure. They were then evaporated to about half volume (40 c.c.), diluted to 100 c.c., nearly neutralised with ammonia, and 100 c.c. of a saturated solution of ammonium carbonate added, which precipitated all the metals except uranium. The solutions were slowly boiled for five minutes, filtered, and the precipitates washed with hot water. The filtrates were evaporated to half volume in order to get rid of most of the carbon dioxide. Yellow precipitates of ammonium uranate separated during boiling, and were dissolved by acidifying the solutions with hydrochloric acid. The solutions were again boiled for about half-an-hour longer, and the uranium determined in four different ways as outlined below.

Solutions Nos. 9 and 10 were precipitated with ammonia in the same manner as solutions Nos. 3 and 4, and the uranium weighed as U_3O_8.

Solutions Nos. 11 and 12 were precipitated by an excess of ammonium dihydrogen phosphate the same as solution No. 5, and the uranium weighed as $(UO_2)_2P_2O_7$.

Solutions Nos. 13 and 14 were evaporated with sulphuric acid, reduced by metallic zinc, and titrated by potassium permanganate as described under Nos. 6 and 7.

In solution No. 15, the filtrate from the ammonium carbonate precipitation was evaporated to dryness with nitric acid, and the uranium determined electrolytically as already described under No. 8.

The results obtained by the ether extraction method are given in Table VIII. (Experiments 9 to 15).

A comparison of these results with those obtained by the Patera separation shows greater uniformity here. The close agreement is proof not only of the superiority of the ether extraction method, but also of the accuracy of the methods of determination of uranium already described.

Summary of Results.

The conclusions drawn from this investigation on the separation and determination of uranium, briefly stated, are as follows:—

1. In order to separate uranium (and the other members of Group 4) from the metals of Groups 5 and 6, the solution should contain not over one part of concentrated acid (either hydrochloric or nitric acid) in fifty parts of solution.

2. The separation of uranium from the metals of Groups 3 and 4 is best accomplished by means of either a saturated solution of sodium carbonate, or else by ether followed by a saturated solution of ammonium carbonate. The latter method is preferable when the introduction of fixed alkalis and silica is undesirable.

3. The ether extraction method for the separation of uranium from iron depends on the fact that ferric chloride is extracted from an aqueous hydrochloric acid solution, whereas the uranyl chloride is retained in the aqueous solution. For this separation it is necessary that the hydrochloric acid used for the solution be of 1·10 specific gravity, and that three ether extractions be made. The ether used should be free from alcohol, and also previously shaken up with hydrochloric acid (sp. gr. 1·10).

4. The separation of uranium from iron by means of sodium carbonate is complete, provided a large excess of a saturated solution of sodium carbonate be used, and the solution boiled for at least fifteen minutes after the precipitation. The boiling is necessary in order to get all the uranium into solution. By such treatment, no uranium remains with the iron, which is completely precipitated as ferric hydroxide in a form readily filtered and washed.

5. The separation of uranium from the alkalis and alkaline earths by means of electrolysis is complete, easily accomplished, and gives accurate results.

6. The separation of uranium from the alkalis and alkaline earths is accomplished by precipitating the uranium three times from a hot solution with ammonia in the presence of ammonium chloride.

7. The separation of uranium from the alkalis and alkaline earths by means of an excess of ammonium phosphate in the presence of ammonium acetate is complete. The precipitations should be made from a hot solution, and the boiling continued for at least fifteen minutes.

8. The yellow slimy amorphous precipitate of an ammonium uranate, formed by precipitating uranium with ammonia in the presence of an ammonium salt, is converted into a darker crystalline form by boiling it for about twenty minutes, and then allowing it to settle in the cold.

9. The separation of the filter-paper from the precipitate of ammonium uranate for the purpose of igniting to UO_2 or U_3O_4 is unnecessary.

10. The complete oxidation of uranium to U_3O_8 is accomplished by igniting ammonium uranate, in either a platinum or porcelain crucible, over a blast-lamp. This is done by having the crucible in a slanting position, and igniting intensely over a blast-lamp for about ten minutes, after which the crucible is allowed to cool in a slowly decreasing Bunsen flame.

11. The reduction of U_3O_8 to UO_2, as recommended by Rose for the purpose of control, was found unreliable.

12. The estimation of uranium as phosphate is easily and accurately done when the precipitant used is ammonium phosphate, in the presence of ammonium acetate. The precipitate of $UO_2NH_4PO_4$ on boiling becomes crystalline, and is easily filtered and washed. The ignited precipitate previous to weighing should be

moistened with nitric acid (sp. gr. 1·42), dried, and re-ignited at low redness in a porcelain crucible. Above this temperature, and especially so in platinum, a reduction of the $(UO_2)_2P_2O_7$ always occurs. Whenever this happens it may be re-oxidised to $(UO_2)_2P_2O_7$ by moistening the greenish mass with nitric acid (sp. gr. 1·42), and re-igniting at low redness. The ignitions should be done in porcelain.

13. The most rapid determination of uranium is accomplished by reducing a sulphate solution by means of pure metallic zinc, and titrating it with standard potassium permanganate solution in an atmosphere of carbon dioxide. The reductions, whether made by means of metallic zinc, aluminum, magnesium, or in a long Jones reductor, were in all cases complete, and the results obtained were concordant with those obtained gravimetrically.

14. When hydrochloric acid solutions of uranium are reduced by means of metallic zinc, aluminum, or magnesium, the reduction goes lower than UCl_4. It approached and in several cases reached the sub-chloride UCl_3. When stannous chloride is used the results are utterly unreliable; so no reduction of uranium in an hydrochloric acid solution can be used for the estimation of uranium.

This work was suggested by Dr. Edmund H. Miller, and carried out under his direction.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 21st, 1901.

Prof. Emerson Reynolds, Sc.D., F.R.S., President, in the Chair.

Messrs. R. Lloyd Whiteley and H. A. Tozer were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Walter Geoffrey Black, 9, Routh Road, Wandsworth Common, S.W.; Harry Burrows, The Green, Southgate, N.; Frederick Edward Catchpole, 11, Jerningham Road, New Cross, S.E.; James Ward Daniels, Westwood, Medomsley R.S.O., Co. Durham; Frederick Davis, "Stanley," Whalley, nr. Blackburn, Lancs.; Charles Dorée, 87, Gore Road, London, N.E.; Clarence J. Green, B.Sc., 24, Dalberg Road, Brixton Church, S.W.; Ernest Bowman Ludlam, University College, Bristol; Sydney Glyde Stephen Panisset, 7, Jersey Road, Strood, Rochester; William Charles Ross, 27, Pitt Street, Edinburgh; Francis Bernard Stead, Clifton College, Bristol; Arthur James Webb, 21, Hammelton Road, Bromley, Kent; Charles Edward Womersley, Kilpin Hill, nr. Dewsbury, Yorks; and of Messrs. T. K. Gajjar, Gingaum, Bombay; J. S. Jameson, Durban, Natal; Albert William Denis Leahy, Darjeeling, India; and Walter Herbert Pay, Durban, Natal, authorised by the Council under By-law I. (3).

Of the following papers, those marked * were read:—

*153. "*On the Hydrochloride of Thiocarbamide.*" By H. P. Stevens.

The hydrochloride of thiocarbamide, CSN_2H_4,HCl, may be obtained directly by dissolving thiocarbamide in an excess of warm concentrated hydrochloric acid. On cooling, the salt separates out in large compact crystals, which have a strongly acid reaction, melting, with decomposition, below 100°, and are readily soluble in water and alcohol. They react with the latter solvent when warmed to form, probably, in the first case, ethyl chloride, which, combining directly with thiocarbamide, yields the hydrochloride of ethyl-pseudo-thiocarbamide in white prisms.

The method of Glutz for the preparation of thiocarbamide hydrochloride yields a very impure product, due partly to loss of hydrochloric acid on concentration, and partly to the salt reacting with alcohol during re-crystallisation.

*154. "*The Constituents of the Essential Oil of Asarum Canadense.*" By F. B. Power and F. H. Lees.

In a previous investigation of this oil by one of the authors (Power, *Inaug. Diss. Strassburg*, 1880; *Proc. Amer. Pharm. Assoc.*, 1880, xxviii., 464) it was found to contain a terpene, $C_{10}H_{16}$; two fragrant alcohols, b. p. 196—199° and 222—226°, both having the composition $C_{10}H_{18}O$; a nearly inodorous body, b. p. 254—257°, which, on oxidation with chromic acid, afforded a crystalline acid, $C_9H_{10}O_4$, the latter having since been shown to be veratric acid by Petersen (*Ber.*, 1888, xxi., 1062), who has also identified the substance affording it as methyl-eugenol; a deep blue oil collected at 275—350°; a large amount of acetic acid combined with the alcohols of the oil in the form of esters, and a very small amount of a less soluble oily acid which was believed to contain valeric acid.

The present investigation has shown the oil to have a much more complex composition than was at first supposed. The authors have now identified the following compounds, most of them by well-defined crystalline derivatives:—(1) A phenol, $C_9H_{12}O_2$, having a creosote-like odour; (2) pinene (nitrosochloride, m. p. 103—104, and nitrolpiperidine, m. p. 118—119°); (3) *d*-linalool (citral and citryl-β-naphtho-cinchoninic acid, m. p. 195—198°); (4) *l*-borneol (camphor, m. p. 175°, $[\alpha]_D = -40·3°$, and oxime, m. p. 115—116°); (5) *l*-terpineol (a ketolactone, $C_{10}H_{16}O_3$, m. p. 62—63°; terebic acid, $C_7H_{10}O_4$, m. p. 173—174°; and dipentene dihydriodide, $C_{10}H_{18}I_2$, m. p. 80°); (6) geraniol (diphenylurethane, m. p. 81—82°, and citral); (7) methyleugenol (bromomethyleugenol dibromide, $C_6H_2Br(OCH_3)_2{\cdot}C_3H_5Br_2$, m. p. 78—79°; it is also shown that methyl*iso*eugenol does not exist in the oil); (8) a blue oil, boiling above 260°, and consisting of oxygenated compounds of undetermined composition but of alcoholic nature; (9) a lactone, $C_{14}H_{20}O_2$, having a very aromatic odour, but present in the oil in very small amount; (10) palmitic acid; (11) acetic acid; (12) a mixture of fatty acids, $C_6H_{12}O_2$ to $C_{12}H_{24}O_2$. The acetic acid is contained in the oil in the form of esters, whilst the higher fatty acids are in a free state.

A quantitative determination of the principal constituents was made. The amount of methyleugenol, determined by Zeisel's method, was found to be 36 g per cent. The amount of esters, calculated as $C_{10}H_{17}{\cdot}C_2H_3O_2$, is 27·5 per cent.; the free alcohols, $C_{10}H_{18}O$, 13·3 per cent. The amount of pinene obtained by direct fractionation of the oil was about 2 per cent, and the amount of high boiling constituents, such as the blue oil, is therefore about 20 per cent.

Discussion.

The President inquired as to the difference between *Asarum* and *Serpentaria*, the *A. Canadense* being known as Canade snake-root, whereas serpentaria was called Virginia snake-root.

Mr. Davis pointed out that Kremers had recently shown (*Pharm. Review*, 1901, xix., 200) that the dark colour of the oil of wild bergamot (*Monarda fistulosa*) is due to small quantities of thymoquinhydrone formed by oxidation from thymoquinol, and asked whether the dark blue colour of the higher boiling-point fractions of the oil obtained by the authors might not be caused by the pre sence of a quinhydrone.

Dr. Power replied that although both *Asarum* and *Serpentaria* belong to the *Aristolochiaceæ*, they are very different, as are also the essential oils obtained from them. The oil from *A. Europæum* differs from that from *A. Canadense* in that the former contains the crystalline sub stance asarone, but apparently none of the alcohols or esters which are present in the latter. With regard to the colour of the oil, the chemical change noted by Kremers in oil of monarda would account for the red or brown

colour of certain oils, but the colour of the blue oils must be attributed to substances of a totally different character.

155. "*On the Oxidation of Sulphurous Acid to Dithionic Acid by Metallic Oxides.*" By H. C. H. Carpenter.

Only two metallic oxides have hitherto been found to react with sulphurous acid so as to produce dithionic acid. These oxides are manganese dioxide and hydrated ferric oxide.

The object of the present research was the investigation of reactions which lead to the formation of dithionic acid, particular care being taken as to the purity of the sulphurous acid and the various oxides used. Dithionic acid is obtained when sulphurous acid reacts with (*a*) hydrated ferric oxide, $Fe_2O_3,3H_2O$, entirely freed from manganese; (*b*) hydrated manganic oxide, Mn_2O_3,H_2O, and (*c*) hydrated cobaltic oxide, $Co_2O_3,3H_2O$, but not with hydrated nickelic oxide, $Ni_2O_3,3H_2O$.

With hydrated ferric oxide, an almost theoretical yield of dithionic acid is obtained. Although it has not been found possible to obtain the theoretical yield of this acid from the corresponding hydrated oxides of mangnese, cobalt, or nickel, yet there is very strong reason for believing, on account of the greater development of energy in the reduction of these oxides, that a partial or even complete decomposition of dithionic acid into sulphuric and sulphurous acids would take place. The facts which point to this conclusion are contained in the two following tables. The first shows the percentages of dithionic and sulphuric acids obtained from the four hydrated oxides already mentioned; the second indicates the changes of energy, expressed in thermal units, involved in the reduction of the oxides.

I.

Hydrated oxides.	Percentage dithionic.	Percentage sulphate.
Ferric	96·06; 96·23	Not estimated
Manganic	75·52; 74·53	25·42
Cobaltic..	36·97; 35·07	63·80; 63·33
Nickelic..	Nil	101·04

II.

Reduction of the hydrated oxides	Heat of reaction.
$Fe_2(OH)_6 = 2Fe(OH)_2 + O + H_2O$	−546 K
$Mn_2(OH)_6 = 2Mn(OH)_2 + O + H_2O$	−448 K
$Co_2(OH)_6 = 2Co(OH)_2 + O + H_2O$	−225 K
$Ni_2(OH)_6 = 2Ni(OH)_2 + O + H_2O$	+ 13 K

A comparison of the two tables shows that the greater the energy required for the reduction of the hydrated oxides, the larger is the percentage yield of dithionic acid. The maximum yield is obtained with ferric hydrate, where the energy that needs to be supplied is such that it is possible to stop the reaction almost wholly at the stage represented by the equation (i.),—

$$Fe_2(OH)_6 + 3SO_2 = Fe_2S_2O_6 + FeSO_3 + 3H_2O.$$

Whether the slight deficit from the theoretical number is due to a slight decomposition of the nature (i.), $FeS_2O_6 = FeSO_4 + SO_2$, or to a defect in the method of estimation used, is a question which it has not been found possible to decide.

In the case of manganic oxide about one-quarter, and in the case of cobaltic oxide about two-thirds, of the dithionic acid formed is decomposed in the manner indicated in equation (ii.).

The reduction of nickelic oxide differs essentially from that of the other three in being an exothermic change, and the energy liberated is such that the reaction cannot be stopped at the intermediate stage, but proceeds wholly to the last stage, and the only oxidation product is sulphuric acid.

The author has confirmed the results of Gay-Lussac and Welter, who showed that no dithionic acid was obtained by the reduction of the peroxides of lead and barium with sulphurous acid. In view of the negative character of these results, the action of sulphurous acid on the dithionates of these metals was studied. It was found that solutions of barium dithionate are quite unaltered, except at a temperature at which the influence of heat alone begins to be seen, when a gradual decomposition into barium sulphate and sulphur dioxide sets in. On the other hand, solutions of lead dithionate are decomposed instantaneously, even at 5°, lead sulphite being precipitated, and free dithionic acid remaining dissolved.

156. "*Optically Active β Hydroxybutyric Acids.*" (Preliminary note). By A. McKenzie.

For certain work the author has been desirous of obtaining *d*- and *l*-β-hydroxybutyric acids. That a substance so simply constituted as externally compensated β-hydroxybutyric acid has not before this been resolved into its optically active components is due to the fact that the salts formed by neutralisation with the common alkaloids are readily soluble and crystallise with some difficulty. The author has resolved the inactive acid, which was prepared by the reduction of acetoacetic ester by sodium amalgam, by means of quinine with water as solvent. After systematic crystallisation, the neutral *l*-acid-*l*-quinine salt was isolated. This salt, which crystallises well, contains $4\frac{1}{2}H_2O$, is very easily soluble in cold ethyl alcohol, moderately so in chloroform, sparingly so in benzene, acetone, carbon tetrachloride, and in ether, and easily in boiling ethyl acetate. An alcoholic solution of the air-dried salt had the rotation $[\alpha]_D\ 15° = -129·9°$ ($c = 2·814$). The anhydrous salt melted at 124·5—125·5°. The *l*-acid from the quinine salt gave $[\alpha]_D\ 16° = -24·9°$ ($c = 8·3304$), whilst the sodium salt prepared from it gave $[\alpha]_D\ 15° = -14·5°$ ($c = 8·518$). These values for the specific rotations of the acid and its sodium salt agree with the values of Magnus-Levy, who obtained the *l*-acid from diabetic urine (*Achiv. für Experim. Path. und Pharmak.*, 1901, xlv., 389).

The author prepared some *l*-acid from diabetic urine by the method of Magnus-Levy, and converted it into quinine salt. The product, when deprived of its water of crystallisation, melted at 124·5—125·5°; an alcoholic solution of the air-dried salt gave $[\alpha]_D\ 15° = -129·0$ ($c = 2·8052$).

Experiments are in progress with the object of isolating the *d*-acid by means of strychnine, the *d*-acid-*l*-strychnine salt being more insoluble in water than the *l*-acid-*l*-strychnine salt.

157. "*Note on the Reduction of Trinitrobenzene and Trinitrotoluene with Hydrogen Sulphide.*" By J. B. Cohen and H. D. Dakin.

By the reduction of 1:3:5-trinitrobenzene and 2:4:6-trinitrotoluene in alcoholic solution with hydrogen sulphide in presence of a trace of ammonia, the corresponding dinitrohydroxylamine compounds are formed, $C_6H_3(NO_2)_3 + 2H_2O = C_6H_3(NO_2)_2NHOH + H_2O$. *Dinitrophenylhydroxylamine* is an orange, crystalline substance, m. p. 114—116°, soluble in alcohol, benzene, and in hot dilute hydrochloric acid; *dinitrotolylhydroxylamine* crystallises from benzene in yellow rhombohedral crystals, and from dilute hydrochloric acid in needles, m. p. 143—145°. Both compounds reduce alcoholic silver nitrate and Fehling's solution; they are slowly decomposed on boiling with dilute, more rapidly with concentrated hydrochloric acid, yielding the amido compounds, and losing oxygen, $C_6H_3(NO_2)_2NHOH = C_6H_3(NO_2)_2NH_2 + O$. In the case of trinitrotoluene, the nitro-group in the ortho-position undergoes reduction, a curious fact, seeing that ammonium sulphide effects the reduction of the para-nitro-group. The 2:4-dinitro-6-toluidine, obtained by the action of strong hydrochloric acid on dinitrotolylhydroxylamine, is a colourless substance, crystallising in needles, and melting at 212—213°.

158. "*The Synthesis of Alkyl-substituted Tricarballylic Acids.*" By W. A. Bone and C. H. G. Sprankling.

The authors have investigated two methods for the preparation of ethyl cyanotricarballylates from succinic acids, as follows;—(1) By the interaction of the sodium compounds of ethyl cyanosuccinates with the esters of

α-bromo-fatty acids, as indicated by the general equation (where R = hydrogen or an alkyl group) —

$$CR_2Br(CO_2Et) + NaC(CN)(CO_2Et)\cdot CR_2(CO_2Et) = = CR_2(CO_2Et)\cdot C(CN)(CO_2Et)\cdot CR_2(CO_2Et) + NaBr,$$

and (2) by the interaction of ethyl monobromosuccinates with ethyl sodiocyanacetate, according to the equation—

$$CR_2(CO_2Et)\cdot CRBr(CO_2Et) + NaCH(CN)(CO_2Et) = = NaBr + CR_2(CO_2Et)\,CR(CO_2Et)\cdot CH(CN)(CO_2Et).$$

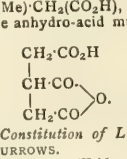
They find that whilst the first method is quite a general one, and affords good yields of ethylcyanotricarballylates, the second has a more limited application (mainly on account of the tendency which ethyl bromosuccinates exhibit to lose hydrogen bromide, and form unsaturated esters), and even in cases where it can be applied, the yields are not so good as those obtained by the first method. The properties of tricarballylic acid itself, and a number of alkyl-substituted acids of the series, their anhydro-acids, and monomethyl salts have been studied. Some of these are indicated in the following table :—

Acid.		M. p.	Dissociation constant.	M. p. of anhydro-acid.
Tricarballylic		157—159	0·022	130—131
α-Methyltricarballylic ..	(1)	179	0 0322	liquid
	(2)	134—135	0·0480	liquid
$\alpha\alpha_1$-Dimethyltricarballylic	(1)	206—207	0 0450	110—112
	(2)	174	0·0545	130
	(3)	143	0 0572	116—117
αα-Dimethyltricarballylic		143	0·0318	135—136
$\alpha\alpha_1$-Di-*iso*propylic	(1)	173	0·1930	liquid
	(2)	156	0·1625	liquid

Monomethyl salts of tricarballylic and αα-dimethyltricarballylic acids have been prepared by three methods, namely, (1) direct partial esterification of the acids, (2) partial hydrolysis of trimethyl salts, (3) the solution of anhydro-acids in methyl alcohol. The products are liquid, but a study of their dissociation constants shows that each of the three methods indicated yields a *single* monomethyl salt, and not a mixture of isomeric monomethyl salts. The dissociation constants of these salts are as follows :—

Acid.	Monomethylic salts by Direct esterification of acid	Partial hydrolysis of trimethylic salt	Solution of anhydro-acid in CH_3OH.
Tricarballic	0·0075	0·00925	0·00945
αα-Dimethyltricarballylic	0·0180	0·00865	0·0186

Since the monomethyl salts obtained by direct esterification of the acids most probably have the formulæ $CH_2(CO_2H)\cdot CH(CO_2H)\cdot CH_2(CO_2Me)$ and $(CH_3)_2C(CO_2H)\cdot CH(CO_2H)\cdot CH_2(CO_2Me)$ respectively (because a carboxyl attached to a *primary* carbon atom is always more readily esterified than one attached to a secondary or tertiary carbon), it follows that the monomethyl tricarballylate obtained by partial hydrolysis of the trimethyl salt, and by solution of the anhydro-acid in methyl alcohol, must have the formula $CH_2(CO_2H)\cdot CH(CO_2Me)\cdot CH_2(CO_2H)$, and therefore that the constitution of the anhydro-acid must be represented thus,—



159. "*Note on the Constitution of Limettin.*" By W. A. Tilden and H. Burrows.

In a previous communication (Tilden, *Trans.*, 1892, lxi., 344), it was shown that limettin, $C_{11}H_{10}O_4$, had the following composition :—

$$C_6H_3{<}\begin{matrix}(OCH_3)_2\\ C_3HO_2\end{matrix}.$$

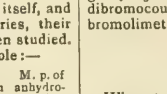
Further experiments have been undertaken with the object of determining the structure of the group C_3HO_2.

In the meantime, the publication of a communication by E. Schmidt (*Apoth. Zeit.*, 1901, lxxi., 619) on a substance which he has isolated from oil of lemon, and has identified with limettin, and the appearance of a recent note by Burgess (*Proc.*, 1901, p. 171) render it necessary to place on record the following results, although at present incomplete.

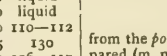
The dibromo-compound previously described by Tilden (*loc. cit.*) melts at 297° with decomposition, and not at 257°.

On treatment with 10 per cent solution of potash, it yields an acid of the composition $C_{11}H_9O_5Br$. Continued treatment with potash does not remove the second atom of bromine.

It is therefore highly probable that the structure of the group C_3HO_2 is similar to that of the ring in coumarin, dibromocoumarin behaving in exactly the same way. Dibromolimettin may therefore be represented as—



When treated with potash, dibromolimettin gives the corresponding *coumarilic acid*,—



from the *potassium* salt of which the *methyl ester* was prepared (m. p. 181°).

On subjecting dibromolimettin to further action of bromine in a sealed tube, a *tribromo*-derivative was prepared containing two hydroxyl groups ; the corresponding *diacetyl* compound melts at 244°.

The following chlorine compounds have been prepared :—

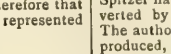
Monochlorolimettin, which melts at 242° and is not acted upon by solutions of alkaline hydroxides. *Dichlorolimettin* melts at 275° and, like the dibromo-compound, with potash gives *monochlorocoumarilic acid*. The trichloro-derivative prepared by Tilden (*loc. cit.*) similarly gives *dichlorocoumarilic acid*.

When limettin is heated on the water-bath with a solution of sodium ethoxide, the *sodium* salt is quickly deposited. Attempts to prepare the methyl derivative were unsuccessful, but when the *silver* salt was heated with a solution of methyl iodide in methyl alcohol, a substance which crystallised in white tufts of needles (m. p. 189°) was isolated, together with re-formed limettin. Analyses showed the substance to have the formula $C_{12}H_{12}O_4$, differing from limettin by CH_2. Its chemical properties are similar to those of limettin, as it readily forms a *bromo*-derivative and a coumarilic acid.

160. "*Derivatives of β-Bromocamphor.*" By H. E. Armstrong and T. M. Lowry, D.Sc.

By heating ordinary αα′-dibromocamphor with hydrogen bromide under certain conditions, it is converted into an isomeric αβ-compound, one of the bromine atoms being transferred from the lateral CBr_2 group. Kachler and Spitzer have shown that this αβ-dibromocamphor is converted by nitric acid into an αβ-dibromonitrocamphor. The authors find that a β-bromocamphoric acid is also produced, isomeric with the acids described by Wreden and by Kipping and Pope. The close resemblance between this β-acid and the isomeric π-acid suggests that the two compounds are similar in constitution—perhaps stereoisomerides ; in other words, that the bromine is present in one of the median methyl groups in the $-CMe_2-$ group of the camphor molecule.

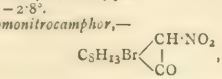
β-Bromocamphoric acid, $C_8H_{13}Br(CO_2H)_2$, softens at about 205° and melts at 208—210°, gas being liberated ; in a 5 per cent solution in alcohol at 10°, $[\alpha]_D = +39{\cdot}7°$. The corresponding *anhydride*,—



crystallises from dilute acetone in long glistening needles ;

t melts at 142°; in a 4 per cent solution in acetone at 10°, $[\alpha]_D = -2{\cdot}8°$.

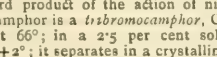
β-Bromonitrocamphor,—



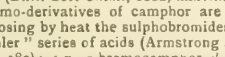
prepared by reducing αβ-dibromonitrocamphor, crystallises from alcohol in short prisms; when heated, it softens at 100° and melts at 112°, but after fusion and solidification re-melts sharply at 100°; being a secondary nitro-compound, it forms salts; and freshly-prepared solutions exhibit the phenomena of mutarotation.

A third product of the action of nitric acid on αβ-dibromocamphor is a *tribromocamphor*, $C_{10}H_{13}Br_3O$, which melts at 66°; in a 2·5 per cent solution in acetone, $[\alpha]_D = +2°$; it separates in a crystalline form on reducing the crude crystalline dibromonitrocamphor, and appears to be identical with the compound obtained by de la Royère by heating αβ-dibromocamphor with phosphorus pentabromide (*Bull. Soc. Chim.*, 1882, xxxviii., 580).

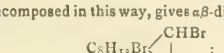
β-Bromo-derivatives of camphor are also obtained on decomposing by heat the sulphobromides derived from the "Reychler" series of acids (Armstrong and Lowry, *Proc.*, 1901, p. 182); *e.g.*, α-bromocamphor-α'-sulphobromide,—



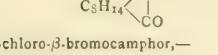
when decomposed in this way, gives αβ-dibromocamphor,—



α-chlorocamphor-α'-sulphobromide,—



gives α-chloro-β-bromocamphor,—



the products obtained being identical with those formed by heating α-bromocamphor and α-chlorocamphor with bromine in sealed tubes.

THE INSTITUTE OF CHEMISTRY.

On Wednesday evening last, the 4th of December, the Annual Dinner of the Fellows and Associates of the Institute of Chemistry was held in the Whitehall Rooms at the Hotel Metropôle. The chair was taken by Professor J. Millar Thomson, LL.D., F.R.S.; the guests numbering about 150. Among those present were Lord Monkswell, Lord Reay, Mr. Hanbury, M.P., the Hon. W. P. Reeves, Professor Rücker, Sir James Crichton Browne, Professor Ramsay, Mr. C. Hawksley, Mr. H. G. Howes, &c.

After the usual toasts of the King, the Queen, and the rest of the Royal Family had been duly honoured, Mr. A. Gordon Salamon proposed the "United Forces," and he took occasion to point out how dependent those forces are upon chemists, both for "quick killing" and food supply in time of war. This toast was responded to by Colonel J. Jocelyn, R.A.

Prof. Ramsay then proposed "The Houses of Parliament" in a very able speech. He first referred to the recent Jubilee of Professor Berthelot in Paris, and laid great stress on the manner in which the French Government had co-operated with the scientific societies to honour this great chemist; he regretted that although the English Government take the advice of the most capable of the scientific men in England on various important points, such as explosives, surgery in warfare, the adulteration of food and drugs, &c., they do not as a rule honour science generally in the persons of those who have most distinguished themselves, as is done abroad. After referring to the importance of the Institute of Chemistry and the value of the degree F.I.C., he touched on the question of the chemistry of water supplies, and gave it as his opinion that, valuable as the bacteriological examination of water may be, it merely confirmed the views of the chemist. He regretted that more chemists are not employed on the Geological Survey, as in the United States, and eulogised the work done by the inspectors under the Alkali Act.

This toast was responded to by Lord Monkswell in an amusing speech, in which he pointed out the manifold advantages of being a member of the House of Lords.

Mr. Hanbury replied for the House of Commons, and he admitted that Government does not always honour science as it should do; he referred to some of the great discoveries which had been made in this country, such as that of aniline dyes, the manufacture of which had gone to Germany, and suggested that salaries were, as a rule, too low in England. Government, he thought, owed a great deal to scientific men, though so few of them had been members of the Privy Council. Agriculture especially was greatly in debt to the chemist, and he thought that no profession required so much all-round knowledge as that of agriculture. He thought, however, that if science could be tempered with practice, and the "hideous terminology," which frightened farmers, done away with, it would be for the ultimate benefit of the country at large. He pointed out the great importance of the discovery of the nodules on leguminous plants which have the faculty of fixing nitrogen from the air, and hoped that further similar discoveries would be made in other branches of agriculture. In this connection he referred to the valuable results obtained by the exporters of butter from Australia, who were now, thanks to a microbe, enabled to land their butter in England in as good condition as that imported from Denmark.

Lord Reay then proposed the "Institute of Chemistry," which toast was ably responded to by the President, who, after referring to the work of the Educational Department, pointed out the importance of the Institute of Chemistry, which though comparatively young had a member-roll of 1040 members, 150 registered students, with 40 more coming up for examination in January next. He urged the necessity of keeping up the high standard of qualifications, combined with the high sense of professional responsibility.

Prof. Wm. Tilden gave "Prosperity to Science and to Scientific Industries," and was proud of the position taken by British men of science. This toast was responded to by Prof. Rücker, who advocated the union of pure and industrial science, which when united will stand, but when divided may fall. Mr. Charles Hawksley also responded to this toast, referring specially to recent work done on the purification of sewage.

The last toast was the "Visitors," proposed by Mr. Friswell, and responded to by Mr. H. G. Howse, President of the Royal College of Surgeons.

The Dehydration of Selenite and the Hydration of Anhydrite.—V. Zunino.—While working with artificial gypsum the author found that the dehydration was complete at 188°. After heating to 230° the product re-absorbs all its water of crystallisation in the presence of steam; if heated to 280° it no longer does so. By melting together a mixture of $CaSO_4$ and NaCl for a few hours, and then letting it cool slowly, he obtained, after levigation, trimetric crystals of anhydrite. It is also possible to obtain this body in small quantities by boiling gypsum for about six hours with a saturated solution of common salt. This anhydrite re-absorbs water, and becomes transformed into gypsum after prolonged contact with water.—*Gazz. Chim. Ital.*, [1], vol. xxx., p. 333.

NOTICES OF BOOKS.

Prospecting for Gold. A Handbook of Practical Information and Hints for Prospectors based on Personal Experience. By DANIEL J. RANKIN, F.R.S.G.S., M.R.A.S. With Illustrations specially Drawn and Engraved for the Work. London: Crosby Lockwood and Son. 1901. Pp. 184.

PROSPECTING for gold has nearly always been carried on in the most haphazard manner by men who worked simply by "rule-of-thumb," or by no rule at all.

A rumour comes down to camp that some one has struck gold away up country, and there is immediately a rush; most of the men know nothing about geology, mineralogy, or mining, but they go on "spec," and sometimes the good thing "comes off," but more often the expedition ends in failure.

The aim of the compiler of this handbook has been to furnish the "intelligent" prospector with information—in a portable form—for which hitherto he would have had to refer to a number of larger volumes. Among the authorities drawn upon we may mention such well-known names as J. D. Dana, Mr. Warnford Lock, Mr. Landauer, Mr. J. A. Miller, &c.

After describing the principal kinds of rocks, the author proceeds to a consideration of their structure, condition, and arrangement, and gives a list of the minerals associated with gold; while special attention is paid to gold in South Africa, and the banket formation.

Methods for the preliminary determination of gold in quartz and ores are given, as well as detailed information with regard to prospecting for alluvial gold, and for auriferous veins and rocks.

It is well known amongst mining men that some of the best paying gold mines are those in which the gold is so finely divided as to be practically never visible in the ores; the prospector should bear this in mind, and not be led away by a few rich specimens, which may possibly contain all the gold for many yards round.

Chapter VIII. is an important one, and contains a large number of tables showing the characteristics of all the principal ores, not only of gold, but of other metals that may be met with, as well as instructions for their preliminary analysis, and special tests. A pocket at the end of the book contains a very useful table, which has been compiled to furnish the prospector with a ready, comprehensive, and clear view of all those characteristics of the mineral ores associated with gold that might facilitate their recognition *in situ*.

This volume is the best we have met with of its kind, and cannot fail to be of service to those for whom it was specially intended.

The Extra Pharmacopœia. By WILLIAM MARTINDALE, F.L.S., F.C.S., and W. WYNN WESTCOTT, M.B.Lond., D.P.H. Tenth Edition. London: H. K. Lewis. 1901. Pp. 688.

SINCE the publication of the last British Pharmacopœia a new edition of the Pharmacopœia Germanica has been published; an Indian and Colonial addendum to the British Pharmacopœia, 1898, and a supplement to the Austrian Pharmacopœia, as well as a revision of the Formulary of the British Pharmaceutical Conference, have also been issued. In preparing this—the tenth edition—the authors have carefully studied all these from the pharmaceutical point of view, as well as noting the current literature, so that they may now be said to present a fair review of the condition of pharmacy and therapeutics at the present time.

Synthetic compounds continue to be in demand, but the chemical products of vegetable origin have not attracted much attention, with the exception of certain morphine derivatives and pilocarpine salts.

Among anæsthetics, ethyl chloride has been found of service, especially by dentists. Bromopin and iodipin have been recommended as nervine sedatives; while peroxide of hydrogen has met with some favour as a germicide in France and America.

Besides these few substances which catch our eye there are, of course, a large number of new remedies which cannot be specially mentioned here; we may, however, add that the whole work has been most carefully prepared, and is worthy of its authors.

Twenty-fifth Annual Report of Her Majesty's Inspectors of Explosives; being their Annual Report for the Year 1900. London: Eyre and Spottiswoode. Edinburgh: Oliver and Boyd. Dublin: E. Ponsonby. 1901. Pp. 209.

THE only modification of the law made during the past year concerning explosives has been an Order in Council in regard to acetylene gas when in admixture with oxygen or air. The full text of the Order will be found in Appendix F, p. 76.

The growth of trade in explosives has continued at an increased rate; this is shown by the greater increase in the number of factories as well as by their increased activity.

The result of 217 visits of inspection show that in the great majority of cases the conditions and management are excellent, and that there has been no falling off in the high standard previously attained. It is, however, to be regretted that at many places the supervision of registered premises by the Local Authority leaves much to be desired.

The number of deaths by accident in manufacture (9) is unfortunately double the average for the decade (4·5), but even this is a low death-rate as compared with that in many other trades.

The number of factories under continuing certificate or licence is 150, but this does not include "toy firework" or "small firework" factories. Four factories have become extinct during the year, while three new ones have been established, and eleven more applications are under consideration.

The total number of persons employed in factories under the Act shows a steady increase as follows:—

Year	1885	1890	1895	1900
No. of persons..	7484	9820	10,023	11,098

It will be seen, in Dr. Dupré's report, that out of 339 samples examined by him, 50 were rejected.

The number of accidents during the year is 77, causing 9 deaths, and injuries to 35 persons; most of these, however, were unimportant, and the injuries sustained slight.

The total number of licensed magazines is now 385, being a decrease of 7; but this decrease is only nominal, being caused by the absorption into factory 156 (Kent) of the 7 magazines owned by the Thames Storage Company.

There has been no modification of the law in regard to the packing of explosives during the year.

There has been a slight rise in the amount of explosives imported during the year, but it is again pointed out that a considerable amount of this is not for home consumption, but is simply brought into this country for re-shipment abroad, and each transaction must be covered by an importation licence, and every cargo sampled and examined, exactly as if it were for home consumption.

Though there are no statutory powers in respect of carbide of calcium or acetylene, except when the latter is in a condition which brings it under the Explosives Act, yet the inspectors are frequently consulted on questions connected with both substances, and, at the request of the Board of Trade, they have prepared a Model Code of Harbour By-laws for carbide of calcium for the assistance of harbour authorities. This code is to be found in Appendix Y, p. 195.

Leitfaden für den Unterricht in der Anorganischen Chemie. By Dr. J. Sperber. Erster und Zweiter Teile. Zürich: E. Speidel.

These two volumes, which comprise the first and second parts of a "Guide to the Study of Inorganic Chemistry," to be followed by a third part, deal with the non-metals and their most important compounds with one another. The book does not claim to be an exhaustive treatise, but it would be hard to find compressed into such small compass more complete and comprehensive accounts of the preparations, properties, and reactions of the various substances treated of. The author's style throughout is concise, clear, and graphic; and the illustrations, which are plentiful, are particularly good. One special feature of the book is the attention paid to structural formulæ, the grounds for which are fully explained; as, for instance, in the case of sulphurous acid. Such explanations, if thoroughly assimilated, will probably very materially simplify for the student the study of organic chemistry. Another point on which the author is to be complimented is the introduction of short explanations and discussions of such theoretical subjects as thermochemical phenomena, dissociation, &c., at appropriate places in the text as suitable examples are met with in illustration of them; such an arrangement tends both to emphasise the facts concerned and to simplify the theory, and is greatly preferable to the more usual method of prefacing the detailed study of the elements with a purely theoretical introduction.

In the second volume, which deals with the oxygen compounds of the metalloids, considerable space is devoted to the commercial process for the manufacture of sulphuric acid; the most recent investigations on the reactions of the chamber gases are fully explained, and an ingenious diagram is given to illustrate the various processes probably occurring in the lead chambers.

The absence of any reference to the periodic system is to be regretted, inasmuch as the law of periodicity serves to throw light upon the relations of the elements of each group among themselves, and of the various groups to one another.

CORRESPONDENCE.

THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

Sir,—The letter which you published on December 6th (Chemical News, vol. lxxxiv., p. 278) from an anonymous "Fellow of the Chemical Society" on the proposed alteration of the meetings of the Society from 8 on Thursday to 5.30 on Wednesday, does not give an accurate idea of the present state of the case. It is true that a post-card vote gave 188 votes in favour of and 78 votes against the change, but I do not believe this vote expressed the real feeling of the Society in the matter. The post-card vote was sprung upon us without any warning, and we were asked to send our vote without delay; several who signed in favour of the change have since altered their opinion. Many thought the change would be against the best interests of the Society, and so a special meeting was summoned by the President to discuss the question; due notice of this meeting was given, and, as far as I know, it was a representative meeting of those Fellows who regularly attend; at all events it was open to everyone who was interested in the question and who chose to take the trouble to be present. Nothing practically was said in favour of the change, and much against it, and as a result, by an almost unanimous vote (99 to 5), it was decided that the change was undesirable.

No one will surely contend that a hastily-taken post-card plebiscite can have any weight when compared with a deliberate and almost unanimous vote taken at a Special Meeting called, after a fortnight's notice, to specially consider the subject.

The object of the meeting on Thursday is practically to protest against the decision of the Council, which is in direct opposition to the wishes of the Society, as expressed at the Extraordinary General Meeting.—I am, &c.,

Frederic Jas. M. Page.

Chemical Laboratory, London Hospital,
December 11, 1901.

FLAME COLOURATION OF NICKEL.

To the Editor of the Chemical News.

Sir,—In a recent report of the transactions of the Chemical Section of the British Association Meeting at Glasgow in September last, I read:—Mr. P. J. Hartog, in describing "The Flame Colouration and Spectrum of the Nickel Compounds," said that nickel acetate produced an evanescent purple tinge, and a persistent red colouration in the Bunsen flame. Professor Smithells remarked that, although experiments with nickel had been made for years, this property had not been observed, and the colouration perhaps might not be due to nickel.

The writer made the same observations in regard to the flame colourations of nickel salts in 1897, and the whole matter was fully discussed in a paper by Professor T. W. Richards and the writer entitled "A Revision of the Atomic Weight of Nickel." This paper was reprinted in the Chemical News (vol. lxxiv., p. 286 *et seq.*).

Gerhardt Krüss noticed a rose-coloured flame in connection with certain nickel compounds as far back as 1889, and believed that it was caused by the presence of an unknown element.

Professor Smithells was therefore mistaken in saying that this property of certain nickel compounds had never been observed.—I am, &c.,

Allerton Cushman.

1526, New Hampshire Avenue,
Washington, D.C., November 18, 1901.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 21, November 18, 1901.

Ammonium Amalgam.—Henri Moissan.—Various chemists have proved the existence of a so-called ammonium amalgam without precisely determining its composition. This amalgam was obtained by acting with pasty sodium amalgam on a saturated solution of ammonium chloride, and the reaction was represented by the equation $NH_4Cl + Na.nHg = NH_4.nHg + NaCl$; the exact value of n never having been determined. The author now finds, in a series of preliminary experiments, that if a solution of the chloride or iodide of ammonium in anhydrous ammonia acts on sodium amalgam, a metallic mass is obtained, in which the hydrogen and ammonia are apparently present in stable combination at a temperature of $-39°$. This metallic mass, when undergoing decomposition at ordinary temperatures in the absence of water, increases to thirty times its volume and evolves two volumes of ammonia gas for one volume of hydrogen.

Compounds of Gold with Chlorine.—Fernand Meyer.—The author's experiments on the possibility of a total transformation of a given quantity of gold into crystallised auric chloride by chlorine, lead him to the conclusion that this transformation can only be accomplished by the action of liquid chlorine, owing to the difference in the solubility of the chloride in cold or hot chlorine.

When thus obtained, the auric chloride is in the form of beautiful crystals. A study of the dissociation of this liquid chloride enables the author to discover the conditions of temperature and pressure which must be used in order to obtain $AuCl_3$ or AuCl. It also shows that a single less chlorinated compound of gold than $AuCl_3$ exists, and this is AuCl. He intends to continue this research to the other halogen compounds of gold.

Dioxyisopropylhypophosphorous Acid.—C. Marie.—The formulæ of the salts and ethers of dioxyisopropylhypophosphorous acid show that it is monobasic, and similar to hypophosphorous acid from which it is derived; also, the existence of diacetyl and dibenzoyl derivatives lead the author to believe that two oxhydriles are present in this acid, and he therefore believes it to possess the following constitution:—

$$\begin{array}{c}(CH_3)_2COH\\|\\POOH.\\|\\(CH_3)_2COH\end{array}$$

Such a body is then the anologue of the dioxybenzylphosphinic acid obtained by M. Ville (*Comptes Rendus*, cviii., p. 659) by the action of aqueous hypophosphorous acid on benzoic aldehyde, and which, from its properties, ought to possess the constitution—

$$\begin{array}{c}C_6H_5CHOH\\|\\POOH\\|\\C_6H_5CHOH\end{array}$$

Action of certain Acid Chlorides on Methyl and Ethyl Sodacetylacetates.—M. Bongert.—In a preceding paper in collaboration with M. Bouveault, the author described his researches on the action of butyryl chloride on methyl sodacetylacetate. He now uses a more general reaction by employing, not only other acid chlorides, but also a different ketonic ether.

Oxidation of Non-saturated Alcohols by the Action of Contact. Preparation of Vanilline.—A. Trillat.—The action of catalytic phenomena, provoked by contact, of certain porous substances at a high temperature can be generalised to non-saturated alcohols of the fatty and also of the aromatic series. Under the influence of the porous material there appears to be a rupture of the molecule, with formation of an aldehyde. Oxidation is even energetic enough to maintain the body in contact in a state of incandescence, as in the case of allylic alcohol. The partial transformation of isoeugenol into vanilline was a particularly interesting result of this investigation.

MISCELLANEOUS.

Subject-matter Index of Mining and Metallurgy.—The Council of the North of England Institute of Mining and Mechanical Engineers will publish shortly a Subject-matter Index of Mining and Metallurgical Literature for the year 1900, and will thereafter continue it yearly. It is expected that it will form a volume of 200 pages, comprising entries of about 8000 separate papers published during the year.

Nitrohydroxylamic Acid.—A. Angeli and F. Angelico.—The salts of this acid were obtained from the sodic salt; viz., the potassium salt $K_2N_2O_3$; the calcium salt $CaN_2O_3{\frac{1}{2}}H_2O$ (dried at 125°), the strontium salt with $1H_2O$ (dried at 110°), and the anhydrous lead salt. Acids decompose these salts quantitatively according to the equation $H_2N_2O_3=2NO+H_2O$. To split it up into nitrous acid and protoxide of nitrogen it suffices to boil the aqueous solution of the soda salt, $2Na_2N_2O_3=2NO_2Na=N_2O+Na_2O$. To split it up into hyponitrous acid and nitrous acid it suffices to melt the sodium salt, $2N_2O_3Na_2=2NaNO_2+N_2O_2Na_2$.

If we treat an aqueous solution of the sodium salt with an aldehyde, the monomolecular hyponitrous acid, HON, which is formed, unites with the aldehyde, giving a hydroxylamic acid. For example, $CH_3COH+NOH=CH_3-C\leqq^{NOH}_{OH}$. — *Gazz. Chim. Ital.*, [1], vol. xxx., p. 593.

Some Reactions of Hydration.—P. Roland.—The author has examined the retarding (or otherwise) action of a number of salts on the solidification of lime, Portland cement, and plaster. The following table gives his results:—

	Lime or Portland cement.	Plaster.
Chloride of sodium	No action	Accelerated
„ lithium	Accelerated	„
„ calcium	„	No action
„ aluminium ..	„	Accelerated
Bichromate of potassium or chromate of calcium ..	Retarded	„
Boric acid or borax	„	Retarded
Carbonate of sodium	Accelerated	„
Sulphate of potassium ..	Retarded	Accelerated

—*Berichte*, xxxiii., p. 2831.

MEETINGS FOR THE WEEK.

MONDAY, 16th.—Society of Arts, 8. (Cantor Lectures). "The Chemistry of Confectioners' Materials and Processes," by W. Jago, F.C.S., F.I.C.

WEDNESDAY, 18th.—Society of Arts, 8. "Range Finders," by Prof. George Forbes, F.R.S.

—— Microscopical, 7.30. An Exhibition on "Development and Structure of Eyes" (illustrated by Micro-slides), by F. W. Watson Baker.

THURSDAY, 19th.—Chemical, 8. "Corydaline—Part VII., The Constitution of Corydaline" and "The Relation of Corydaline to Berberine—The Oxidation of Berberine with Nitric Acid," by J. J. Dobbie and A. Lauder. "The Magnetic Rotation of some Polyhydric Alcohols, Hexoses, and Disaccharoses," by W. H. Perkin, F.R.S. "Stereoisomeric Halogen Derivatives of α-Benzoylcamphor," by M. O. Forster and F. M. G. Micklethwait. "Is Argon an Elementary Substance?" by G. Martin.

DR. A. ISBERT, Technical Business,
FRANKFORT-ON-MAIN, GERMANY.
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ST. PAUL'S SCHOOL.—An Examination will be held at St. Paul's School, West Kensington, on Tuesday, January 14th, 1902, and following days, for filling up about Four Vacancies on the Foundation.—Full particulars can be obtained from the Bursar.

COVERS FOR BINDING.
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THE CHEMICAL NEWS.

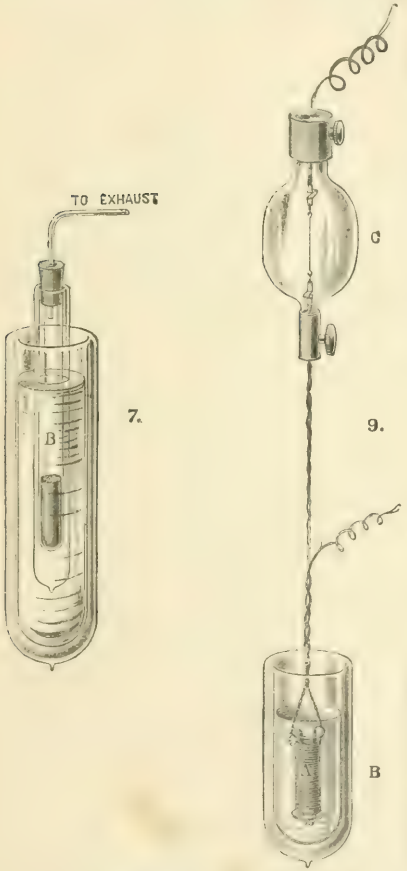
VOL. LXXXIV., No. 2195.

SOLID HYDROGEN.*

By Professor DEWAR, M.A., LL.D., D.Sc., F.R.S.

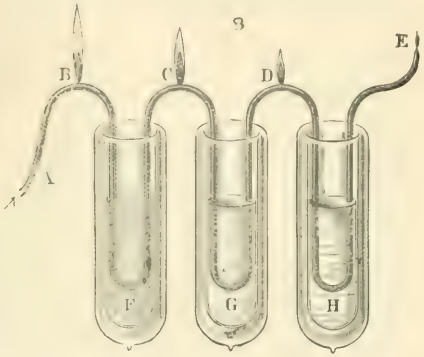
(Concluded from p. 282).

FOR the lecture demonstration of solid hydrogen the apparatus may be most conveniently arranged as is shown in Fig. 7. The small vacuum tube B, after being filled

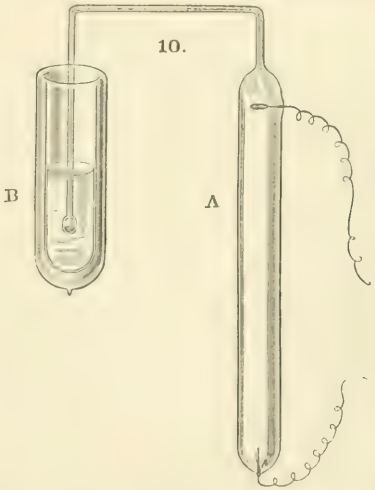


7. 9.

with liquid hydrogen, is immersed in a larger vessel of the same kind filled with liquid air. By this arrangement the rate of the liquid hydrogen evaporation is so much diminished that it does not exceed that of liquid air in the same vessel when used in the ordinary way. On gradually applying exhaustion to the liquid hydrogen it is forced from its effective heat isolation to pass to a lower temperature, and when the exhaustion reaches 50 m.m. the mass suddenly begins to solidify into a froth-like material.



In order to ascertain the appearance of the hydrogen, made by cooling the liquid produced in a hermetically closed vessel, the following experiment was arranged. A flask of about a litre capacity, to which a long glass tube was sealed, A, B, Fig. 5, was filled with pure dry hydrogen and sealed off. The lower portion B of this tube was cali-



brated. It was surrounded with liquid hydrogen placed in a vacuum vessel arranged for exhaustion. As soon as the pressure of the boiling hydrogen got well reduced below that of the atmosphere, perfectly clear liquid hydrogen began to collect in the tube B, and could be observed accumulating until the liquid hydrogen surrounding the outside of the tube suddenly passed into a solid white

* A Discourse delivered before the Royal Institution, April 6, 1900.

foam-like mass, almost filling the whole space. As it was not possible to see the condition of the hydrogen in the interior of the tube B when it was covered with a large quantity of this solid, the whole apparatus was turned upside down in order to see whether any liquid would run down from B into the flask A. Liquid did not flow down the tube, so the liquid hydrogen with which the tube was partly filled must have solidified. By placing a strong light on the side of the vacuum test-tube opposite the eye, and maintaining the exhaustion at about 25 m.m., gradually the hydrogen froth became less opaque, and the solid hydrogen in the tube B was seen to be a transparent ice, but the surface looked frothy. This fact prevented the solid density from being determined, but the maximum fluid density has been approximately ascertained. This was found to be 0·086, the liquid at its boiling-point having the density 0·07. The solid hydrogen melts when the pressure of the saturated vapour reaches about 55 m.m. In order to determine the temperature of solidification two constant volume hydrogen thermometers were used. One at 0° C. contained hydrogen under a pressure of 269·8 m.m., and the other under a pressure of 127 m.m. The mean temperature of the solid was found to be 16° absolute under a pressure of 35 m.m. All the attempts made to get an accurate electric resistance thermometer for such low temperature observations have been so far unsatisfactory. Now that pure helium is definitely proved to be more volatile than hydrogen, this body, after passing through a spiral glass tube immersed in solid hydrogen to separate all other gases, must be compared with the hydrogen thermometer. Taking the boiling-point as 21° absolute under 760 m.m., and the similar value under 35 m.m. is 16° absolute, then the following approximate formula for the vapour tension of liquid hydrogen below one atmosphere is derived :—

$$\log p = 6{\cdot}7341 - 83{\cdot}28 / T \text{ m.m.},$$

where T is the absolute temperature, and p the pressure in m.m. This formula gives for 55 m.m. a temperature of 16·7° absolute. The melting-point of hydrogen must therefore be about 16° or 17° absolute. It has to be noted that the pressure in the constant volume hydrogen thermometer, used to determine the temperature of solid hydrogen boiling under 35 m.m., had been so far reduced that the measurements were made under from one-half to one-fourth the saturation pressure for the temperature. When the same thermometers were used to determine the boiling-point of hydrogen at atmospheric pressure, the internal gas pressure was only reduced to one-thirteenth the saturation pressure for the temperatures. The absolute accuracy of the boiling-points under diminished pressure must be examined in some future paper. The practical limit of temperature we can command by the evaporation of solid hydrogen is from 14° to 15° absolute. In passing it may be noted that the critical temperature of hydrogen being 30° to 32° absolute, the melting-point is about half the critical temperature. The melting-point of nitrogen is also about half its critical temperature. The foam-like appearance of the solid when produced in an ordinary vacuum vessel is due to the small density of the liquid, and the fact that rapid ebullition is substantially taking place in the whole mass of liquid. The last doubt as to the possibility of solid hydrogen having a metallic character has been removed, and for the future, hydrogen must be classed among the non-metallic elements.

All solid bodies by themselves make very unsatisfactory cooling agents unless we can use them to cool some liquid. Now, with solid hydrogen we can cool no liquid other than hydrogen, so that, for effective cooling, we must use the liquid just above its freezing-point, which is about 16°. It will, however, take a long time to exhaust the wide field of investigation which the use of liquid hydrogen opens up; so we may proceed to illustrate some of its further applications. In former lectures the relation of electrical resistance to temperature has been discussed, and it was experimentally demonstrated that the curves of resistance of the pure metals all pointed to this quality disappearing or becoming exceeding small at the absolute zero. This fact has been confirmed, even with the most highly conducting metals, down to the lowest temperature we can command. The experiment illustrated in Fig. 9 shows to an audience the diminution of resistance of pure copper wire when cooled in liquid hydrogen, in contrast to liquid air. An incandescent lamp C has been placed in circuit with a fine coil of copper wire A, immersed in liquid air, the resistance being so adjusted that the filament in C is just visible when the current passes under these conditions. Now, on removing the coil from the liquid-air vessel and placing it in another similar vessel filled with liquid hydrogen, a great increase in the brilliancy of the lamp is observed. As a matter of fact, the sample of copper has its resistance in liquid air reduced to about one-twentieth of what it is at the temperature of melting ice, whereas in liquid hydrogen the resistance is reduced to one-hundredth of the same amount. In other words, the resistance in liquid hydrogen is only about one-fifth of what it is in liquid air. The interesting point, however, is that theoretically we should infer, from experiments made at higher temperatures, that at a temperature of −223° C. the copper should have no resistance, or it should have become a perfect conductor. As this is not the case, even at the temperature of −253°, we must infer that the curve co-relating resistance and temperature tends to become asymptotic at the lowest temperatures.

Liquid hydrogen is a most useful agent for the production of high vacua and for the separation of gases from air that may be more volatile than oxygen or nitrogen. An experiment illustrating the production of a high vacuum is shown in Fig. 10, where A is the large electric discharging tube to which has been attached a narrow glass tube twice bent at right angles, and terminating in a bulb at the end for immersion in the liquid hydrogen. The raidity with which the vacuum is attained is shown by the rate at which the striation in the tube changes and the phosphorescent state supervenes. Another rough illustration of the application of cold to effect the separation of a complex mixture of gases is shown in Fig. 8. Coal-gas is passed in succession through the U-tubes F, G, and H made of ordinary gaspipe, having small holes at B, C, D, and E, in order that a flame may be produced before and after each vessel is passed. Each of the U-tubes is placed in a vacuum vessel, and the first cooling substance the gas in its transit meets is solid carbonic acid in F, then liquid air in G, and finally liquid hydrogen in H. At the temperature of the carbonic acid bath, all the easily condensable hydrocarbons separate, and consequently the flame C is less luminous than B. The liquid air bath condenses the ethylene and a large part of the marsh gas, and allows the carbonic oxide and the hydrogen to pass through, so that flame D is less luminous than C. Finally, after the liquid hydrogen bath, nothing escapes condensation but free hydrogen, the carbonic oxide and any marsh gas being solidified; the result is, the flame E is almost invisible.

A really practical application of liquid hydrogen is the purification of helium obtained from the gases emitted by the mineral springs of Bath. Although the helium only amounts to one-thousandth part by volume—the nine hundred and ninety-nine being chiefly nitrogen—yet the low temperature method of separation can be successfully applied.

Now that we know definitely the approximate values of some of the more important physical constants of liquid hydrogen, it is interesting to look back at the values that have been deduced—say for such a constant as the density—by various workers using entirely different methods. The following table gives some of the more important values of the density of hydrogen under the different conditions in which it enters into organic and inorganic bodies.

Density of Hydrogen in Different Conditions.

Kopp	Organic bodies	0·18
Amagat	Limit of gaseous compression	0·12
Wroblewski ..	Van der Waals's equation ..	0·027*
Van der Waals..	Superior limit of density ..	0·82
Graham	Palladium alloy	2·0
Dewar	Palladium alloy	0·63
Dewar	Liquid hydrogen at B.P. ..	0·07

* Critical density.

My density at the boiling-point agrees substantially with that which can be deduced from Wroblewski's form of the Van der Waals' equation. The deduced densities of Kopp for organic bodies and Amagat for gaseous compression are both about the same value, and may be taken as a mean to be twice the observed density of hydrogen in the liquid state. The conclusions of Graham and myself, touching the density of the hydrogen in the so-called alloy of palladium, must be regarded as altogether exceptional. Even my value would exceed the density of the stuff constituting the real gas molecule, according to the theory of Van Der Waals. In order to harmonise the palladium hydrogen results with those deduced from the study of organic bodies, we must assume that, during the formation of the so-called hydrogenium, a condensation of the palladium sufficient to increase its density by one-fifth must take place. This is by no means an unreasonable hypothesis. The mode of determining the density of hydrogen at its melting-point has been previously described and found to be 0·086. In the same way the approximate values for the densities of nitrogen and oxygen at their melting-points have been found, their respective values being 1·07 and 1·27. The following table shows the comparison between my results and those given by Amagat for high gaseous compressions :—

Densities.

	Liquid Melting-point.	Gas, 3000 atmospheres.	Limiting value, 4000 atmospheres.
Hydrogen ..	0·086	0·097	0·12
Nitrogen ..	1·1	0·833	0·12
Oxygen ..	1·27	1·127	1·25

It will be noted that the density of gaseous hydrogen at 3000 atmospheres is actually greater than the maximum density of the liquid state; but neither in the case of nitrogen nor oxygen does the density at the same pressure reach the fluid density. Amagat's limiting value for oxygen under 4000 atmospheres would, however, be almost identical with mine.

During the course of my inquiries sufficient data have been accumulated to construct Waterston Formulæ giving the approximate densities of liquid hydrogen, nitrogen, and oxygen in each case through a wide range of temperature. The equation for each substance is given in the following table :—

Liquid Atomic Volumes,

Hydrogen = 23·3 − 8·64 log (32° − *t*)
Nitrogen = 30·0 − 11·00 log (127° − *t*)
Oxygen = 32·6 − 10·22 log (155° − *t*)

	Absolute Zero.	Observed at Melting-point
1. Atomic volume of hydrogen }	= 10·3	11·7
2. ,, ,, }		
3. ,, nitrogen ..	= 12·8	13·1
4. ,, oxygen ..	= 10·20	12·6

From these formulæ we find the respective hypothetical atomic volumes of hydrogen, nitrogen, and oxygen at the absolute zero to be 10·3, 12·8, and 10·2. My observed minimum fluid volumes were 11·7, 13, and 12·6. The coefficients of expansion of the liquids, taken in the same order at their respective boiling-points, are 0·024, 0·0036, and 0·0046. Thus liquid hydrogen has a coefficient of expansion five times greater than that of liquid oxygen. Further inquiry will enable the constants in these equations to be determined with greater accuracy. In the meantime, however, they give us general ideas of the order of magnitude of the quantities involved.

I have to thank Mr. Robert Lennox for efficient aid in the arrangement and execution of the difficult experiments you have witnessed. Mr. Heath has also heartily assisted in the preparations.

ON THE SILICO-VANADIO-MOLYBDATES.

By C. FRIEDHEIM and C. CASTENDYCK.

Preparation of Silico-vanadio-molybdate of Ammonium—800 grms. of yellow silico-molybdate of ammonium $2(NH_4)_2O.SiO_2.12MoO_3+8H_2O$ are put in suspension in 1·5 litres of water; this is then heated to boiling-point on the water-bath, and, gradually, 180 grms. of white vanadate of ammonium, VO_3NH_4, are added, and allowed to dissolve completely.

The resulting very deep red solution is evaporated down to 1 litre at the lowest possible temperature, and finally to dryness in a desiccator.

It first of all deposits brilliant red crystals, very soluble in water, then microcrystalline crusts or felted masses of a yellow or brownish-red colour, only slightly soluble in water. The first body is a silico-vanadio-molybdate; as it cannot be re-crystallised in water without alteration it must be separated mechanically from the other products. These other salts are vanadio-molybdates :—

Microcrystalline Crusts—

$2(NH_4)_2O.2V_2O_5.5MoO_3+8H_2O$ ..	Yellow.
$(NH_4)_2O.V_2O_5.2MoO_3+4H_2O$ ..	Yellowish green.
$2(NH_4)_2O.3V_2O_5.4MoO_3+11H_2O$.	Yellowish brown.

Felted Needles—

$(NH_4)_2O.2V_2O_5.2MoO_3+8H_2O$ ..	Reddish brown.
$4(NH_4)_2O.12V_2O_5.5MoO_3+24H_2O$	Brownish red.

Analysis of the Silico-vanadio-molybdate.—After having heated very carefully to drive off the water and the ammonia, the material is calcined in a combustion tube in a current of hydrochloric acid gas; oxychlorides of vanadium and molybdenum are thus volatilised and collected in an absorption apparatus full of water. But as this volatilisation would never be really completed, the operation is interrupted, and the calcination finished in a current of air, which peroxidises the lower oxides of vanadium and molybdenum which may have been formed. If the calcination in hydrochloric acid gas is then continued, the metals are entirely volatilised, and pure silica is left in the boat. The contents of the absorption tube are treated with sulphuretted hydrogen under pressure, which completely precipitates the molybdenum as MoS_3, quite free from vanadium, and easy to estimate as MoO_3. As for the estimation of the vanadium, the simplest method is to make another determination on a fresh sample in the hydrochloric solution, also containing molybdenum, estimating the vanadium by the iodometric method, according to Friedheim and Euler (*Berichte*, vol. xviii., p. 2061).

Composition and Properties of the Silico-vanadio-molybdate of Ammonium.—By the above method the composition of this body is found to be—

$$3(NH_4)_2O.SiO_2.V_2O_5.11MoO_3+27H_2O.$$

Dilute hydrochloric and sulphuric acids decompose it partially with a deposit of silica or the other microcrystalline salts; ammonia also reacts on it, giving a deposit of silica, and decolorising the solution. The salts of the heavy metals give coloured precipitates, often crystalline; the salts of barium give, after a time, crystals containing ammonia and barium with the three acids. Pure water also decomposes silico-vanadio-molybdate of ammonium. By evaporating the solution other salts were obtained,

only differing in composition from the original salt by the number of molecules of MoO_3 and of water :—

$3(NH_4)_2O.SiO_2.V_2O_5.9MoO_3+20H_2O$,
$3(NH_4)_2O.SiO_2.V_2O_5.10MoO_3+21H_2O$,
$3(NH_4)_2O.SiO_2.V_2O_5.15MoO_3+24H_2O$.

The salts containing $9MoO_3$ and $15MoO_3$ can be recrystallised in water without change; the others have a tendency to become transformed into these latter under the action of water. They all give special precipitates with the salts of the heavy metals.

When treated in cold saturated solution with a saturated solution of potassic chloride they give orange-coloured precipitates, in which two-thirds of the ammonia are replaced by potassium :—

$(NH_4)_2O.2K_2O.SiO_2.V_2O_5.9MoO_3+20H_2O$,
$(NH_4)_2O.2K_2O.SiO_2.V_2O_5.10MoO_3+21H_2O$,
$(NH_4)_2O.2K_2O.SiO_2.V_2O_5.11MoO_3+12H_2O$,
$(NH_4)_2O.2K_2O.SiO_2.V_2O_5.15MoO_3+14H_2O$.

—*Berichte*, vol. xxxii., p. 1611.

VOLUMETRIC DETERMINATION OF ALUMINA FOR TECHNICAL PURPOSES.

By C. R. GYZANDER.

THE method to be described makes no claim of being original, but does give with ease practically correct results, in a very short time comparatively speaking. It is based on these simple reactions—

$$Al_2(SO_4)_3+6NaOH=Al_2(OH)_6+3Na_2SO_4$$

and—

$$Al_2O_3+3H_2SO_4=Al_2(SO_4)_3+3H_2O.$$

Many observers have found that a correct determination of the sulphuric acid in sulphate of alumina is not possible when using normal caustic soda solution, on account of the formation of basic salts, which render the results too low. My own observations corroborate these results and show also that it is useless to employ a factor for correction, as the relation between acid and base, in the salt thrown down by the caustic soda, differed greatly under different conditions. To overcome this difficulty, it has been proposed to convert the sulphate into chloride, by adding an excess of barium chloride solution. Though correct results may be obtained in this way, it offers no particular advantage, because, if the titration is carried on in the presence of the barium sulphate thrown down, the end-point is very obscure, the results much too high and seldom twice alike. Separating the barium sulphate by filtration gives sharp end-point, but it consumes a good deal of time and introduces a source of error from incomplete washing. Without entering into details of experiments which led to the adoption of the following method, I will at once state that, when using a solution of caustic soda not over one-third normal, the results are in accord with the reactions quoted. Though the results are equally good with sulphates, chlorides, and nitrates, the present article treats exclusively of the sulphate, of which three distinct varieties are met with in trade. First, sulphates made from pure, artificial, hydrate of alumina; second, sulphates made from bauxite; and third, sulphates containing zinc sulphate. The first is practically pure sulphate of alumina, containing only a very small amount of silica and sodium sulphate with a mere insignificant trace of iron. The second contains in addition to sulphate of alumina, ferrous and ferric sulphate, mixed or singly. The third contains, in addition to what has already been mentioned, zinc sulphate, and all three are liable to contain copper or arsenic or both, and are either normal, technically termed neutral, basic, or acid. Reagents needed for the analysis are, caustic soda solution free from aluminate and carbonate, and distilled water free from carbon dioxide and ammonia, together with methyl-orange and phenolphthalein as indicators. By using *caustic soda made from sodium* and manufactured by a reliable firm, an alkali free from alumina may be obtained, and from this one may readily eliminate any carbonates present by treatment with barium hydrate solution, shaking and settling. The clear liquid is then carefully titrated and diluted to the required strength. An aqueous solution of sulphuric acid, of the same strength as the caustic soda solution, is also needed.

As pure potash alum formed the experimental material, its preparation will now be described. I may, however, first remark that the results here reported are based on common atomic weights, and potash alum, in consequence, contains 10·85 per cent $Al_2(SO_4)_3$. According to the more recently revised atomic weights, potash alum contains 10·77 per cent $Al_2(SO_4)_3$, but, although this lower figure may be more correct, the difference of 0·08 per cent. is, for all practical purposes, negligible.

Preparation of Pure Potash Alum.

A hot, saturated, and filtered solution of best procurable potash alum is left to crystallise, the mother-liquor poured off, the crystals washed with some cold water, and a hot saturated solution again made from these crystals in a beaker, which is then placed in a dish of cold water, and the liquid is stirred while cooling. A crop of small crystals is the result. These are drained in a glass funnel, with perforated platinum cone, by means of a suction-pump. When no more water drops off the funnel, the alum is transferred to a sheet of white filter-paper and pressed, until no more wet spots appear on the paper; then transferred to another filter-paper, placed on a warm radiator, and moved about with a horn spatula, until it has the appearance of a perfectly dry, sandy white powder. The alum was transferred to a dry glass stoppered bottle for use.

Determination of Water in the Alum.

1·3099 grms. were weighed in a covered platinum crucible and mixed with recently and strongly ignited pure lime, then covered with some more lime, the crucible cover put on, and the weight ascertained. The crucible was then heated to dull redness over a Bunsen flame and kept so for 15 minutes. It was then cooled in a desiccator and the loss in weight ascertained. The heating was continued for another 15 minutes, after which it was again cooled and weighed. The weight remained constant and the loss of water was 0·5961 grm., or 45·51 per cent, indicating that the alum was pure.

Of this alum, quantities equivalent to 10 grms. of from 50 to 100 per cent $Al_2(SO_4)_3$ were weighed and dissolved in a litre of distilled water, and furnished solutions containing known quantities of pure $Al_2(SO_4)_3$.

Standard Caustic Solution.

This was made by diluting the previously mentioned, purified and settled, caustic soda solution so that one litre contained 11·65 grms. of NaOH. I will refer to this as *standard soda solution*. 100 c.c. neutralise exactly 3·7862 grms. acid sodium oxalate $NaHC_2O_4+aq$. with phenolphthalein as indicator. I prefer this salt to oxalic acid, as it is easily prepared pure and, unlike oxalic acid, is unalterable in air or over sulphuric acid. I prepare it as follows:—To a hot, saturated, and filtered solution of pure oxalic acid was added a hot, saturated, and filtered solution of pure sodium carbonate, so proportioned that there was a slight excess of oxalic acid over what was required for the acid oxalate. The precipitated salt was drained by suction, in a funnel, pressed between filter paper, and dried over sulphuric acid in a desiccator.

Another caustic soda solution, so diluted that 100 c.c. neutralised 1·1370 grms. of acid sodium oxalate, with phenolphthalein as indicator, was also made, and will be referred to as *dilute standard soda solution*.

With the standard soda solution the burette reading corresponds to per cent Al_2O_3, and with the dilute

standard to per cent" $Al_2(SO_4)_3$, when half a grm. of sulphate is used for the titration.

Sulphuric acid of such strength that 100 c.c. neutralised an equal volume of standard soda solution was also made and will be referred to as *standard acid*.

One grm. methyl orange dissolved in one litre of water will be referred to as methyl in licator, while one grm. of phenolphthalein in 500 c.c. alcohol will be referred to as phenol indicator.

Analysis of Hydrate Sulphate.

Dissolve 10 grms. of the salt to be tested in boiling water and filter; wash the filter thoroughly, dry and incinerate it, and determine insoluble. Cool the filtrate, and make it up to 1 litre with distilled water; mix thoroughly by shaking; use 50 c.c. for the titration, and add 2 drops of methyl and 4 drops of phenol indicator, 2 c.c. standard acid, and 100 c.c. distilled water; run in standard soda solution slowly, drop by drop and with constant stirring, for some time between each addition of caustic, until the colour changes from pink to orange, not yellow.

If the sulphate was normal, it will require exactly 2 c.c. standard soda solution; if it was basic, then the excess of alumina will form sulphate with the sulphuric acid added, and, in consequence, less than 2 c.c. of standard caustic will be required to neutralise the solution. In that case, the difference between the sulphuric acid and standard soda used gives per cent of basic alumina. Continue to run in standard soda solution (starting from 0 of the burette) in a moderate stream and with constant stirring, until a faint but permanent pink is obtained. The number of cubic centimetres of standard soda solution used indicates per cent total Al_2O_3. From it, subtract the basic and multiply the remainder by 3·33, and the result is per cent $Al_2(SO_4)_3$.

The correct end-point for neutrality with methyl-orange, for sulphates up to 60 per cent $Al_2(SO_4)_3$, is obtained by comparison with the tint of a solution of 50 c.c. pure potash alum (10 grms. per litre), to which is added 2 drops of methyl indicator and 100 c.c. distilled water. The following solutions were made:—

	Grms. per litre.		Per cent $Al_2(SO_4)_3$.		Per cent Al_2O_3.
1.	10	=	36·13	or	10·85
2.	13·8389	=	50·00	,,	15·01
3.	15·2228	=	55·00	,,	16·51
4.	16·0531	=	58·00	,,	17·41
5.	16·6066	=	60·00	,,	18·01
6.	19·3744	=	70·00	,,	21·02
7.	22·1422	=	80·00	,,	24·02
8.	24·9100	=	90·00	,,	27·02
9.	27·6778	=	100·00	,,	30·03

Each of these solutions were tested with *standard* and *dilute standard* soda solution.

To 50 c.c. of each solution were added 2 drops methyl, 4 drops phenol indicator, and 100 c.c. distilled water. The caustic solution was run in, in a rapid succession of drops and with constant stirring, until pink began to appear; then slowly, drop by drop, until a faint—but distinct and permanent—pink was obtained, and which did not fade after continued stirring.

The phenol end-point is sharpest at about 30° C. Above this temperature, the results are incorrect and in excess of the theoretical amount, as alumina at high temperatures is acid towards phenolphthalein. Below 20° C. the reaction is very tardy, and the end-point, in consequence, obscure.

Towards the end of the reaction, the precipitated alumina forms with phenolphthalein a pink-coloured lake, which persists even after the most vigorous stirring; methyl-orange masks this pink colour, and thus helps to sharpen the phenol end-point. This residuary colour becomes more troublesome at low temperatures and with strong sulphates, and for that reason I add 3 drops of methyl indicator to sulphates with over 60 per cent $Al_2(SO_4)_3$. The results recorded below are the average of five determinations.

	Standard.			Dilute standard.	
	Found. Al_2O_3.	Calculated. $Al_2(SO_4)_3$.	Error.	Found. $Al_2(SO_4)_3$.	Error.
1.	10·84	36·10	−0·03	36·05	−0·08
2.	14·96	49·82	−0·18	49·90	−0·10
3.	16·48	54·88	−0·12	54·84	−0·16
4.	17·34	57·74	−0·26	57·88	−0·12
5.	17·94	59·74	−0·20	59·88	−0·12
6.	20·88	69·53	−0·47	69·92	−0·08
7.	23·88	79·52	−0·48	79·92	−0·08
8.	26·84	89·38	−0·62	90·08	+0·02
9.	29·82	99·30	−0·70	99·94	−0·06

From these figures, it will be seen that the dilute standard gives better results, but that, for practical purposes, the *standard* is correct for sulphates up to 60 per cent $Al_2(SO_4)_3$.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 5th, 1901.

Mr. C. E. Groves, F.R.S., Vice-President, in the Chair.

Messrs. George Harker and T. G. Donnan were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Harry Burrows, The Green, Southgate, N.; Kenneth Macomb Chance, Lawnside, Edgbaston; William Clifford, 1, Avondale Road, Wolverhampton; John Kemp Smith Dixon, Gothic House, Birstall, nr. Leeds; Alfred Vincent Elsden, Storrington, Pulborough, Sussex; Lewis Eynon, 57, Darenth Road, Stamford Hill, N.; Frederick Ferrand, 13, Torrington Street, Hopwood, Heywood; John Oliver Ferrier, Colombo, Ceylon; George Frederick Holdcroft, 253, Oxford Street, Manchester; Frank Sturdy Sinnatt, Glenside, Church Lane, Moston, Manchester; Lyon Viccars Turner, Crescent Lodge, St. John's, S.E.

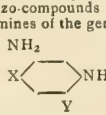
A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Messrs. Frederick T. Allen, B.Sc.; Arthur Baker; Thomas Thorne Baker; Walter Craven Ball, B.A.; Andrew Russell Bennett; Harding Bickford; Henry Boyers; William Burton, B.Sc.; William Cormack; Samuel Irwin Crookes; Frank Crossley; John Howard Davidson, B.Sc.; Francis Davis; Robert English; Henry Whippell Gadd; T. K. Gajjar, M.A., B.Sc.; Hermann Charles T. Gardner; Edward Gillman; William Peer Groves, B.A.; Herbert Blackmore Hammond; Herbert Harding; Edwin Hobson; Beresford Ingram, B.A.; J. S. Jameson; Charles H. Johnson, M.B., Ch.M.; Walter Henry Jollymann; James David Kettle, B.Sc.; J. Bruce-Kingsmill, M.A., B.Sc.; Alfred Tabois Larter; Albert W. D. Leahy; Peter MacDonald; Charles K. Millard, M.D., D.Sc.; Edward Holl Miller; Christian Müller; Herbert Simpson Newbould; Albert Edward Parkes; Walter Herbert Pay; Charles James Tomlin Pollitt; Rowland Samuel Potter; Charles Leonard Royle; John Henry Ryffel, B.A., B.Sc.; Allan Sandford; George Charlton Scott; Edward Charles Sherwood, M.A.; Norman Smith, B.Sc.; Robert Stephenson, jun., B.A.; William Henry Templeman; Harold Foy F. Varley; Frank Wade; Morton Wager; Herbert George Wallace; Philip Lewington Whitehouse.

Of the following papers, those marked * were read:—

*161. "*Influence of Substitution on the Formation of Diazoamines and Ammonium-compounds.*" By G. T. Morgan, D.Sc.

The disubstituted derivatives of *m*-phenylenediamine having one free para-ortho-position with reference to the

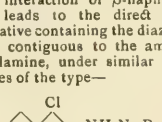
amino-radicles interact readily with diazonium salts, giving rise to aminoazo-compounds in almost theoretical quantities. The diamines of the general formula—



having substituents in both the para ortho-positions do not easily condense with diazonium salts, and the yield of aminoazo-compound is very poor.

The bases of both series, however, combine with primulin diazotised on the cotton fibre, the diamines of the first series giving rise to reddish-brown azo-compounds, whilst those of the second series furnish colouring matters having a brownish-yellow tint.

Although the interaction of β-naphthylamine and a diazonium salt leads to the direct formation of an *o*-aminoazo-derivative containing the diazo-residue $R{\cdot}N_2-$ in the *o*-position contiguous to the amino-group, yet 1-chloro-2-naphthylamine, under similar conditions, yields stable diazoamines of the type—



In this compound, the azo-group has no tendency to shift into the aromatic nucleus, this transference being apparently prevented by the presence of the chlorine atom in the adjacent ortho-position.

The following acyl derivatives were prepared in characterising certain of the diamines employed in this investigation. *Diformyl-4 : 6-diamino-1 : 3-xylene*, needles, m. p. 182—183°, the corresponding *diacetyl* and *dibenzoyl* derivatives, m. p. respectively at above 260° and 253°; *diformyl-2 : 4-diamino-1 : 3 xylene*, m. p. 219—220°, the *diacetyl* derivative, m. p. above 260°, and the *dibenzoyl* derivative, m. p. 232°; *diformyl-5 chloro-2 : 4-tolylenediamine*, silky needles, m. p. 166°, the *benzoyl* derivative, m. p. 205°.

The following azo-compounds were produced in illustrating the behaviour of the two series of diamines towards diazonium salts. *Benzene-5-azo-2 : 4-diamino-1 : 3-xylene*, readily produced from 2 : 4-diamino-1 : 3-xylene, brown needles, m. p. 208—209°; its *diacetyl* derivative, m. p. above 260°; *diacetylbenzene-5-azo-2 : 4-tolylenediamine*, m. p. 216—217°.

Benzene-5-azo-4 : 6-diamino-1 : 3-xylene, obtained with some difficulty and in small yield from 4 : 6-diamino-1 : 3-xylene, forms deep red plates, m. p. 182—183°; its *diacetyl* derivative, m. p. above 260°. *p-Toluene 5-azo-4 : 6-diamino-1 : 3-xylene* resembles its lower homologue, and melts at 165—166°. Small yields of *benzene-3-azo-5-chloro-2 : 4-tolylenediamine* and its *p-toluene homologue* are produced from 5 chloro-2 : 4-tolylenediamine; they crystallise in dark, brownish-red plates, m. p. 147° and 152° respectively; the *dibenzoyl* derivative of the former azo-compound melts at 236—237°.

Benzene 6-azo-2-chloro-3 : 5 tolylenediamine, obtained in theoretical quantity from 2 chloro-3 : 5-tolylenediamine, forms orange-red, acicular prisms, m. p. 134°; its *diacetyl* and *dibenzoyl* derivatives crystallise in orange coloured needles, m. p. 251° and 233° respectively.

1-Chloro-2-naphthylamine yields the following diazoamines when treated with the appropriate diazonium chloride. *2-Diazoamino-1-chloronaphthalene*, $ClC_{10}H_6{\cdot}N_3H{\cdot}C_{10}H_6Cl$, produced by the action of 1-chloro-2 naphthalenediazonium chloride, crystallises in golden-yellow needles, m. p. 152°.

p-Nitrobenzene-2-diazoamino-1-chloronaphthalene, $NO_2{\cdot}C_6H_4{\cdot}N_3H{\cdot}C_{10}H_6Cl$, obtained from *p*-nitrobenzenediazonium chloride and 1-chloro-2-naphthylamine, or from 1-chloro-2-naphthalenediazonium chloride and *p*-nitraniline, crystallises in brownish-yellow leaflets; it melts and decomposes at 197—198°. Its production by the two processes indicated shows that Kekulé's rule for the formation of mixed benzenoid diazoamines applies also to those containing naphthalene residues. The *ethyl* derivative, produced by the direct ethylation of the preceding compound, separates from benzene in hard, yellow, prismatic crystals, m. p. 193—194°.

Discussion.

Mr. Evershed asked whether the primulin compounds described were only obtainable on the fibre, and if so, whether similar compounds could be obtained outside the fibre by using dehydrothioparatoluidine instead of primulin.

Dr. Hewitt inquired whether the author expected to obtain three distinct ethyl derivatives of unsymmetrical diazoamino compounds, or whether the derivative obtained by alkylation would not be a mixture of the other two ethyl derivatives obtained by coupling diazotised amines with monoethylamines. Such cases had already been observed by Meldola. The earlier idea that in the benzene series *p*-azo-compounds exclusively result when the para-position is free can no longer be held to be absolutely true. Bamberger (*Ber.*, 1900, xxxiii., 3188) has obtained small quantities of ortho-oxyazobenzene mixed with a large amount of the para-isomeride by the action of a phenyldiazonium salt solution on an alkaline solution of phenol.

Dr. Morgan, in reply, said that the colouring matters produced from diazotised primulin were obtained only on the cotton fibre, this reaction being employed merely as a ready means of ascertaining whether the symmetrically disubstituted diamines react with diazo-compounds. The substances prepared by the action of the simpler diazonium salts (benzendiazonium chloride and its *p*-tolyl homologue) on these bases have the appearance of true azo-compounds; they are readily acetylated and benzoylated without decomposition, and withstand prolonged digestion with boiling hydrochloric acid, either in aqueous or alcoholic solutions, just like the isomeric azo-derivatives obtained from the diamines, in which the diazo-residue enters the ring in a para ortho-position with respect to the amino-radicles.

*162. "*The Determination of Available Plant Food in Soils by the Use of Dilute Solvents.*" By A. D. Hall and F. J. Plymen.

The use of various weak acid solvents has been suggested in the analysis of soils, as dissolving out the mineral plant food which may be regarded as immediately "available" for the crop.

In order to ascertain which acid would give the most "critical" results as judged by the known history of the soil, the authors have determined the phosphoric acid that could be extracted from nineteen different soils by a 1 per cent solution of citric acid, by equivalent solutions of hydrochloric and acetic acids, by a saturated solution of carbonic acid, and by an ammoniacal solution of ammonium citrate respectively. Seven of the soils were from plots on the Broadbalk field, Rothamsted, which had been continuously manured in the same manner for forty-two years previously; the remaining twelve were soils of very various origin, which had been the subject of crop experiments, and of which the reaction to phosphatic manuring was well marked. In the same seven soils from the Broadbalk field the authors determined the potash extracted by the same solvents, with the exception of ammonium citrate; five other soils of different origin, whose response or otherwise to potash manuring had been tested by experiment, were also examined. Determinations were made of the phosphoric acid and potash dissolved after long digestion with strong hydrochloric acid, of the loss on ignition, and of the earthy carbonates present in each soil.

The acids did not attack the phosphates and potash in the same way; in the case of phosphoric acid most was dissolved by citric acid, in the case of potash by hydrochloric acid; water charged with carbonic acid generally

dissolved less than the other solvents. In all cases the weak acids gave better indications of the need of the soil for special mineral manuring than was afforded by the determination of the total phosphoric acid or potash present.

Though, as a rule, all the acids gave similar indications as to the relative fertility of the soils, as regards the mineral matters under consideration, certain differences exist in their modes of attack; for example, from the soil of the Broadbalk field, which had received an annual dressing of dung for forty-two years, the weak hydrochloric acid extracted a comparatively smaller proportion of phosphoric acid than the other solvents; hydrochloric acid again had relatively slight action on the phosphates of the nitrated plots. The strength of the acids used affected the amount of phosphoric acid dissolved, and the addition of calcium carbonate to the soil diminished the amount dissolved by citric, but not by acetic or carbonic acids.

Though the differences in the rate of attack which the various acids exhibit in dealing with soils of a different type are related to the varying states of combination of phosphoric acid or potash in the soils, there is still sufficient likeness in the indications afforded by all the acids to negative the idea that any one acid can be found which will discriminate sharply between the "available" and "non-available" mineral plant food.

The authors conclude:—

1. That no sharp distinction can be drawn between "available" and "non-available" phosphoric acid and potash in the soil, and that any process for determining the "available" constituents is an empirical one, dependent on the strength and nature of the acid used.

2. That the weak solvents give information as to the requirements of a given soil for mineral manures of a far more trustworthy nature than that which is afforded by such a solvent as strong hydrochloric acid.

3. That of the acids examined, the 1 per cent solution of citric acid gives results most in agreement with the recorded history of the soil, though there is evidence that the same interpretation cannot be put on results obtained from all types of soil.

Discussion.

Dr. Armstrong said the only way in which the method advocated could be tested was to compare the laboratory results with those afforded by field experiments such as had been made at Rothamsted; and it was remarkable how general was the agreement in that case. But he felt less happy after listening to the account given of this work with other soils; the results did not appear to be so uniformly in favour of Dr. Dyer's method. The conditions offered by soils were obviously very complicated, and it was difficult to believe that so simple a test could afford really comparable results in all cases, especially when applied to soils varying greatly in character. But the case was one in which the decision must be based on considerable experience. Dr. Armstrong took exception to the authors' use of curves in expressing their results, and suggested that only vertical ordinates should be plotted.

Mr. T. S. Dymond said that this paper was particularly interesting, as one of the soils was a London clay from the "derelict" grass land of Essex, from a field which manurial trials had shown to be almost devoid of available phosphoric acid. When superphosphate of lime was used, a dressing of nitrate of soda had doubled the produce of hay, while in its absence nitrate of soda failed to give any increase at all. The citric acid-soluble phosphoric acid in the top nine inches of soil amounted, as shown by the authors, to 200 lbs. per acre, while the crop was able to remove no more than 2 lbs., leaving, apparently, no further available phosphoric acid in the soil. Although that quantity might be potentially "available" in the soil, it was not actually available in such land as this, until, by improving its mechanical condition, air was admitted, fermentation encouraged, and carbonic acid produced. The experiment also indicated that the acidity of the root sap of the grasses and clovers had little, if any, effect in dissolving "available" phosphate. Both on this ground and on the ground that the carbonic acid-soluble phosphoric acid, as shown by the authors, was much lower than the citric acid-soluble phosphoric acid, the use of carbonic acid as a solvent would appear to give a truer idea of the amount of phosphoric acid actually available. No conclusion as to the manurial requirements of such land should be drawn without also taking into account the various circumstances favourable to carbonic acid production.

Mr. F. J. Lloyd said that, as in the case of Dr. Dyer's paper (*Proc.*, 1894, x., 36), no steps seemed to have been taken to allow for the alkaline reaction of the soil. In the 200 grms. used by the authors there might easily be present 4 grms. of calcium carbonate, a quantity which would materially affect the 20 grms. of citric acid in 2 litres of solution, so that the soil was not really subjected to the action of a 1 per cent solvent.

Mr. Hall said, in reply, that the effect produced by calcium carbonate in the soil had not been overlooked. The authors had used a soil to which successive additions of 2, 5, and 10 per cent of calcium carbonate were made before treating with the dilute acid. The amount of phosphoric acid dissolved by the citric acid was diminished with each addition of calcium carbonate, but the attack of acetic and carbonic acids was practically unchanged. The diminution was not, however, proportional to the neutralisation of the acid, because neutral saline solutions themselves had a solvent effect, dissociation doubtless coming into play.

There were discrepancies still to be cleared up in the results furnished by citric acid; probably as was indicated in the paper, for different types of soil different "limits" would have to be taken as indicative of the need of mineral manures.

•163. "*On a Method for Determining Small Quantities of Carbonates.*" By A. D. Hall and E. J. Russell.

The authors have devised an apparatus for determining small quantities of carbonates in material like soil by measuring the carbon dioxide evolved. The material is placed in a small bulb, the volume of which need not be known, in which the pressure is reduced to an approximate vacuum; the carbonate is decomposed by the admission of dilute sulphuric acid, and the change in pressure thus produced is noted. Connection is then made with a second vacuous bulb of known volume, and the change in pressure again read. From the two changes in pressure the volume of carbon dioxide can be calculated. A knowledge of the volume of the material is not required, and the volume of the carbon dioxide which dissolves in the reacting liquid does not enter into the calculation, since the liquid practically forms part of the unknown volume of the first bulb.

Examples are given of the measurements of carbon dioxide evolved from pure carbonates in known quantity ranging from 0·13 c.c. to 11·26 c.c.

164. "*Derivatives of Gallic Acid.*" By F. B. Power and F. Shedden.

The authors have prepared and described the following derivatives of gallic acid:—

Ethyl dinitrodiacetylgallate,—

$$C_6(NO_2)_2(C_2H_3O_2)_2OH{\cdot}CO_2C_2H_5,$$

was prepared by the nitration of ethyl triacetylgallate, m. p. 133°. It forms lemon-yellow needles, m. p. 165°.

Ethyl dinitrotriacetylgallate,—

$$C_6(NO_2)_2(C_2H_3O_2)_3{\cdot}CO_2C_2H_5.$$

was prepared from the preceding compound by the action of acetic anhydride. It forms colourless needles, m. p. 145–146°, which gradually become yellow. Its cold alcoholic solution gives no reaction with ferric chloride, but, on boiling, a bluish green colour is produced.

Ethyl dinitrogallate, $C_6(NO_2)_2(OH)_3{\cdot}CO_2C_2H_5$.—When an alcoholic solution of ethyl dinitrodiacetylgallate is

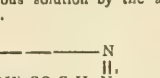
boiled with sodium ethoxide, and allowed to stand, the *sodium salt of ethyl dinitrogallate* was deposited as a bright red, crystalline powder. From the aqueous solution of the latter, hydrochloric acid precipitates ethyl dinitrogallate in the form of small yellow scales, which melt at 153—154°. The same compound was obtained by boiling ethyl dinitrodiacetylgallate with 50 per cent sulphuric acid.

Ethylmonamidogallate hydrochloride,—

$$(C_6H(NH_2)(OH)_3{\cdot}CO_2C_2H_5,HCl,H_2O,$$

was obtained, together with the diamido-derivative, by the reduction of ethyl dinitrogallate with tin and hydrochloric acid. It forms white, needle-shaped crystals, which melt at 210° with decomposition. It can be precipitated from its aqueous solution by the addition of strong hydrochloric acid.

Diazoethylgallate,—



$$C_6H(OH)_2CO_2C_2H_5{\cdot}N$$

was obtained by the action of nitrous acid on ethyl monamidogallate. When recrystallised from dilute acetic acid it forms fine, reddish-brown needles, which melt with sudden decomposition at 182°. When heated with water in a sealed tube at 220° for four hours, the nitrogen is completely eliminated, and ethyl gallate is produced.

Ethyl diamidogallate hydrochloride,—

$$C_6(NH_2)_2(OH)_3{\cdot}CO_2C_2H_5,2HCl,$$

was obtained, together with the above described monamido-derivative, by the reduction of ethyl dinitrogallate. It melts with decomposition at 197°, and is very easily oxidised. It dissolves readily in water, and the solution almost immediately becomes blue, the colour being intensified by the addition of a very little ferric chloride, but destroyed by an excess.

165. "*Note on Phosphorus Suboxide.*" By K. C. BROWNING, M.A.

The author has investigated the following methods used to prepare so-called phosphorus "suboxide."

1. Oxidation of phosphorus, both in the solid state and in solution, by air diluted with carbon dioxide.

2. Action of metals on phosphorus oxychloride.

3. Action of acetic anhydride on sodium hypophosphite.

The results obtained confirm, on the whole, those of Chapman and Lidbury, and of Burgess and Chapman, although the author believes that the suboxide *can* exist under certain conditions.

166. "*The Bromination of Trimethylsuccinic Acid and the Interaction of Ethyl Bromotrimethylsuccinate and Ethyl Sodiocyanacetate.*" By W. A. BONE and C. H. G. SPRANKLING.

When trimethylsuccinic acid is heated under pressure to 130° with the calculated quantity of bromine, it is converted into the characteristic white *bromotrimethylsuccinic anhydride*, m. p. 197—198°. On the other hand, if the bromination be carried out according to the Hell-Volhard-Zelinsky (phosphorus and bromine) method, and the product be poured into alcohol, a mixture of the bromoanhydride and *ethyl bromotrimethylsuccinate* results, from which it is difficult to obtain the latter substance in a tolerably pure state.

On heating the bromoanhydride with diethylaniline hydrogen bromide is eliminated, and on afterwards pouring the liquid into a solution of potassium hydroxide, the potassium salt of *methylenedimethylsuccinic acid*, $(CH_3)_2C(CO_2H){\cdot}C(CO_2H){\cdot}CH_2$, is obtained. The acid melts at 140—141°, its diethyl salt boils at 173—176° (755—760 m.m), and readily absorbs bromine and hydrogen bromide in the cold.

Ethyl bromotrimethylsuccinate reacts with ethyl sodiocyanacate with the formation of the cyano-ester, which on hydrolysis yields a tribasic acid, $C_9H_{14}O_6$, melting at 137—138°. This acid is not *i*-camphoronic (*aa*8-trimethyltricarballylic) acid (m. p. 169—173°), which would have resulted had the reaction proceeded normally, thus:—

$$(CH_3)_2C(CO_2Et){\cdot}C(CH_3)Br(CO_2Et)+ \\ +NaCH(CN)(CO_2Et)= \\ =(CH_3)_2C(CO_2Et){\cdot}C(CH_3)(CO_2Et){\cdot}CH(CN)(CO_2Et)+ \\ +NaBr.$$

Most probably the acid is the isomeric *aa-dimethylbutane aa'β-tricarboxylic acid*, a view which the authors' experiments so far justify, and its formation is explained on the supposition that ethyl bromotrimethylsuccinate, in contact with ethyl sodiocyanacetate, loses hydrogen bromide, forming ethyl methylenedimethylsuccinate, which immediately condenses with ethyl cyanacetate as indicated by the equation:—

1. $(CH_3)_2C(CO_2Et){\cdot}C(CH_3)Br(CO_2Et)= \\ =HBr+(CH_3)_2C(CO_2Et){\cdot}C(CO_2Et):CH_2.$

2. $(CH_3)_2C(CO_2Et){\cdot}C(CO_2Et):CH_2+CH_2(CN)(CO_2Et)= \\ =(CH_3)_2C(CO_2Et){\cdot}CH(CO_2Et){\cdot}CH_2{\cdot}CH(CN)(CO_2Et).$

The further investigation of the new acid is now being prosecuted.

167. "*β-Bromocamphor.*" By H. E. ARMSTRONG and T. M. LOWRY.

The formation of derivatives of β-bromocamphor on decomposing by heat the sulphobromides of the Reychler series of substituted camphorsulphonic acids has been described in a previous notice (*Proc.*, 1901, p. 217). On treating the unsubstituted sulphobromide in a similar manner, in the spring of the present year, a bromocamphor was obtained, which melted at 76°, very similar to ordinary bromocamphor; but as the melting-point of a mixture of the two substances was 65°, it was clear that they were not identical. By further purification of the substance, the melting-point was raised to 79°. The optical rotatory power of the new compound is very different from that of α bromocamphor, a solution in acetone containing 3·3 per cent giving $[\alpha]_D = 18°$, the corresponding value for the α-bromocamphor being 143°.

Recently, larger quantities of material have been prepared, and proof has been obtained that the new bromocamphor is the parent term of the β-series by its direct oxidation into β-bromocamphoric acid.

Simultaneously with the authors, Dr. M. O. Forster has obtained β-bromocamphor by simply brominating the isomeride of camphor which he has described under the name of hydroxycamphene. A direct comparison of the products from the two sources has been made, which leaves no doubt as to their identity. Dr. Forster's observations are described independently.

168. "*β-Bromocamphor.*" By M. O. FORSTER.

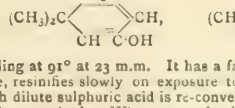
When 1-hydroxycamphene (*Trans.*, 1901, lxxix., 644), dissolved in glacial acetic acid containing sodium acetate (1½ mols.), is treated with a solution of bromine (1 mol) in the same solvent water precipitates a new bromocamphor, which, from the fact that bromine converts it readily into β-dibromocamphor melting at 114°, must be regarded as the monobromocamphor which has the substituent in the unknown β-position. The bearing which this observation has upon the constitution of 1-hydroxycamphene will be discussed in a future communication.

β-Bromocamphor, $C_{10}H_{15}OBr$, crystallises from alcohol in long, colourless, prismatic needles, and separates from petroleum in transparent, well-formed prisms; it melts at 78°, has $[\alpha]_D = +19°$ in alcohol, and $[\alpha]_D = +16°$ in chloroform. Alcoholic potash eliminates bromine from the substance, and converts it into an unsaturated acid which belongs probably to the campholenic series. The *oxime* crystallises from alcohol in lustrous, rhomboidal plates, which melt at 156°.

169. "*Substituted Dihydrobenzenes.*" Part I. By A. W. CROSSLEY and H. R. LE SUEUR.

When 2 : 6-diketo-4 : 4-dimethylhexamethylene (dimethyldihydroresorcinol) is treated with phosphorus pentachloride, both oxygen atoms are removed apparently

as hydroxyl groups, giving rise to 2 : 6-*dichloro* 4 : 4 *dimethyldihydrobenzene*, a colourless, highly refractive liquid,—



boiling at 91° at 23 m.m. It has a faint odour of turpentine, resinifies slowly on exposure to air, and on boiling with dilute sulphuric acid is re-converted into dimethyldihydroresorcinol. When treated with sodium in moist ethereal solution, both chlorine atoms are replaced by hydrogen atoms, and there results 4 : 4-*dimethyldihydrobenzene*, a clear, colourless, mobile liquid, with a marked odour of turpentine, boiling at 111°. It is homologous with the terpenes, which it resembles in chemical behaviour. Thus it decolorises a solution of bromine in chloroform; concentrated sulphuric acid produces a blood-red colour, changing to violet on standing, and with hydrogen bromide it gives a crystalline *hydrobromide*.

Its properties are being thoroughly investigated, and other similar hydrocarbons are being prepared.

170. "*The Part Played by Residual Affinity in the Formation of Substitution Derivatives. The Orienting Influence of Sulphur.*" By H. E. ARMSTRONG and E. HORTON.

In previous notices, it has been argued that the formation of ortho- and para-substitution derivatives from phenolic and aminic compounds is due to the attractive influence exercised by the oxygen and nitrogen respectively, and experimental evidence has been adduced which shows that if the phenolic or aminic hydrogen be displaced by hydrocarbon or acid radicles, the "activity" of the oxygen or nitrogen is more or less diminished, if not entirely destroyed; in other words, that the "residual affinity" of the negative element becomes weakened in some cases to the point of being inoperative (compare *Proc.*, 1899, xv., 176; 1900, xvi., 157; *B. A. Report*, 1899, 683).

Although applied to the explanation of the formation of substitution derivatives generally as far back as 1887 (*Trans.*, li., 268), the doctrine of "residual affinity" has not hitherto received the attention it perhaps deserves in this connection; we seem to heve forgotten that the conception that addition precedes substitution dates back at least to Kekulé's famous paper on the valency of carbon (1858). But now that the doctrine of residual affinity has been re-discovered in Germany by Thiele, and advocated by von Baeyer (*Ber.*, 1901, xxxiv., 2686), it appears likely to become the fashion, and there is some chance that at last justice may be done to the peculiar qualities of the negative elements; the tendency at the moment to credit oxygen with full tetrad functions is proof, however, that unless care be taken the doctrine will be pushed to unwarrantable extremes.

In studying the influence of residual affinity, sulphur is an element of peculiar interest deserving of far more attention than it has hitherto received; its lethargic behaviour in benzenoid compounds is especially remarkable. To obtain further knowledge of these compounds, the authors are engaged in contrasting the thiobenzenoid ethers with the corresponding oxygen ethers.

Methyl and ethyl phenylsulphides are readily sulphonated, yielding para-acids, which afford well-defined salts, &c. On oxidation by permanganate, the thiosulphonates are converted into corresponding sulphone-sulphonates. If an aqueous solution of the thiosulphonate be subjected to the action of bromine, it is converted wholly into the corresponding sulphoxide-sulphonate; for example, $EtS\,C_6H_4{\cdot}SO_3K + B_2 + OH_2 = EtSO\,C_6H_4{\cdot}SO_3K + 2HBr$, the bromine acting only as an oxidising agent. As it was probable that oxidation was due to the formation of hypobromous acid, in the expectation that if this were prevented from forming, bromine would be without action, the salt was brominated in presence of muriatic acid; under these conditions, the salt was converted entirely into the ortho-bromo-thiosulphonate. It seems, therefore, that, if prevented from undergoing oxidation, sulphur may behave as oxygen does; but the thioether-sulphonates are far more stable than the oxygen-ether-sulphonates, as the sulpho-group is not displaced from them by bromine.

Mr. Lewis has ascertained that muriatic acid has, in some cases, a distinct influence on the course of change on brominating the oxygen-ether-sulphonates, and that it promotes the formation of the ortho-bromosulphonate whilst diminishing the extent to which the sulphonic group is displaced.

Library Catalogue.

A new Catalogue of the Library, arranged under authors' names and subjects in accordance with the system adopted in indexing the Society's publications, is ready for the press. Fellows who desire a copy of the catalogue, at a cost of 2s. 6d., are requested to send in their names to the Secretaries not later than January 31st, 1902.

If a sufficient number of names is not received, the catalogue will not be printed.

Memorial Lectures, 1893—1900.

Fellows can now obtain copies of the volume of collected Memorial Lectures on application to the Assistant Secretary, price 7s. 6d. post free.

PHYSICAL SOCIETY.

Ordinary Meeting, December 13th, 1901.

Prof. S. P. THOMPSON, President, in the Chair.

THE following papers were read by the SECRETARY:—

"*On Circular Filaments or Circular Magnetic Shells equivalent to Circular Coils, and on the equivalent Radius of a Coil.*" By Prof. T. R. LYLE.

It is shown that we can represent the magnetic action of any coil by replacing it by one or more filamentary circuits in which currents circulate bearing a simple relation to the actual current in the coil. It the axial and radial dimensions of the coil in question are the same, then the external magnetic action can be represented by that of one filamentary circuit. If the axial breadth is greater than the radial depth we must employ two filaments of equal radii separated by an axial distance; and if the opposite condition holds, two circular filaments of different radii lying in the same plane perpendicular to the axis of figure of the coil. In the case of coils in which the axial and radial dimensions are equal, a modification of Bosscha's method is described which yields the equivalent radii directly as the result of length measurements. If the axial and radial dimensions are not equal, it is shown that the method is still applicable provided that the ratio of the resistances of the Bosscha comparison be altered in a ratio depending on these dimensions. Apparatus for carrying out the experiment is described, and applications to some classical cases are given. It is also pointed out that the correction for finite length of magnet in Bosscha's (or the present) method of comparison is in general far from negligible. The formulæ used are based on the expansion of the potential of a coil for points on its axis and terms up to the fourth have been included, but the effect of neglecting higher terms is not investigated.

The SECRETARY read a letter from Lord Rayleigh in which he stated that the length of the magnet used in determining the constant of the current balance used in the determination of the electrochemical equivalent of silver was one-tenth of an inch, and the error due to neglecting this was less than one part in ten thousand.

Mr. W. WATSON expressed his interest in the method because it reduced the ordinary arithmetical calculations,

and drew attention to some advantages of the practical applications.

The CHAIRMAN said it was a useful step to reduce the action of a rectangular coil to that of two filaments. In the case of a tangent galvanometer with one coil, if the channel is cut to take nine turns axially and eleven radially, then the equivalent radius is equal to the mean radius.

"On *Air-pressures used in Playing Brass Instruments.*" By Dr. E. H. BARTON and Mr. S. C. LAWS.

It is well known that in playing upon the "brass" or "woodwind" instruments of the orchestra, the particular note, at any instant desired, is produced by the simultaneous use of the mechanism of the instrument and the corresponding "embouchure" through which air at a suitable pressure is driven by the performer. The object of the paper is to find how the air pressure required to sound the different notes varies with (1) the pitch of the note (2) its loudness, (3) the fingering or other manipulation of the instrument, (4) on the instrument itself. Experiments were made with the tenor trombone, the trumpet, and the cornet, and the pressures were taken by a water-manometer connected to the performer's mouth by an india-rubber tube terminating in a glass nozzle which could be held by the side teeth. The following inferences are drawn from the experiments:—(1) Other things being equal, the louder the note the greater the pressure. (2) The higher the pitch of the note played on a given instrument the greater the air-pressure used. (3) The curves formed by plotting the logarithms of the frequencies of the notes as abscissæ and the pressures as ordinates are straight lines. (4) The air-pressure required to sound any note with given intensity is approximately proportional to its pitch defined logarithmically. (5) Where alternative positions or fingerings are used for the same note the pressures are practically the same. (6) The pressures for identical notes on trumpet and cornet are almost the same for any given intensity, but very much less than those for the same notes on the trombone. (7) The pressures used for loud low notes may exceed those for soft high notes.

Prof. J. D. EVERETT said the paper was an interesting attempt to make a quantitative connection between theory and practice, and the linear law connecting logarithmic frequencies and pressures came out well from the experiments. He asked if the pressure necessary depended on the skill of the operator.

Mr. D. J. BLAIKLEY said that soon after the publication of Dr. Stone's experiments on this subject he followed up the matter by experiments of his own, using a simple water-pressure guage. The general results agreed fairly well with those given in the paper, but from them one law appeared to be deducible which was not suggested by Dr. Barton and Mr. Laws, and which greatly modified their conclusion (4). His observations showed that when the intensity was reduced to the lowest possible point for each of the notes in a given series, the resulting minimum pressures were directly proportional to the frequencies and not to the frequencies as defined logarithmically. It was further noticed that whether a given note—as, say, B♭ of 240 vibrations—was sounded as the eighth harmonic of a contrabass, the fourth harmonic of a tenor trombone or euphonium, or as the second harmonic of a cornet, the result was approximately the same. The minimum pressure at which any note can be sounded appeared to depend solely upon its absolute pitch and not upon the place of the note, upon the instrument used, or upon the calibre or total mass of air in the instrument.

Mr. WATSON suggested that if different gases were used to blow the instruments the results might depend upon the velocity of sound in the gas used.

"*On a New Hygrometric Method.*" By Mr. E. B. H. WADE.

In this method a thermometer is wetted, not with water but with sulphuric acid of such a strength that the temperature of the acid bulb is close to that of the dry bulb. The maximum tension of the acid at any temperature is known from Regnault's work, and two or more determinations with this instrument and with a wet and dry bulb hygrometer at the same time enable the constants of both instruments to be determined. If the difference between the acid bulb and the dry bulb is less than 2° the constant remains fixed over a large range. Experiments show that the readings of the instrument are not affected by ventilation, and since the difference between the temperatures of the bulbs is small errors in the determination of the constant are unimportant.

Prof. J. D. EVERETT criticised the paper at length and said he could not commend the method described.

Prof. A. S. HERSCHEL said that tables might be constructed for use with the author's instrument similar to those used by Glaisher with the ordinary wet and dry bulb hygrometer.

Mr. W. WATSON replied to some of Prof. Everett's remarks, and pointed out some of the advantages of the method described in the paper.

The Society then adjourned until January 24th, 1902.

NOTICES OF BOOKS.

The Elementary Principles of Chemistry. By A. V. E. YOUNG. New York: D. Appleton & Co., 1901. Pp. 358.

THE arrangement of this volume is as remarkable as it is confusing. It is apparently divided into two parts; the first part called "The Elementary Principles of Chemistry," extends to 252 pages, including an index of eight pages. The book is properly paged, but this paging is entirely useless, as no reference to any page number is made either in the index or the table of contents, or "Scheme of Topics," as the author prefers to call it; on the other hand, the whole book is divided into numbered paragraphs, and it is these latter figures which have been used in both cases for reference.

Having rounded off the first 252 pages, the author skips two and begins again in Part II., called "Experimental Illustrations," with a fresh series of page and paragraph numbers from one onwards, extending to p. 106; but, on p. 90 the paragraph numbers stop at 601, to be resumed on p. 91 at 1 again; they then continue to the end, where they reach par. 23.

When we further add that the second part is included in the index in the middle of the volume, it may perhaps be conceived what a tangle the whole thing is in.

In spite of a certain amount of merit in the descriptions and general language used, we are sorry we cannot recommend this book. The two parts should have been intelligently combined into a homogeneous whole; in its present shape, the student would be half his time turning from the index in the middle to one or the other ends, if he was really anxious to follow that excellent rule of letting theory go hand in hand with practice.

CORRESPONDENCE.

VOLUMETRIC ESTIMATION OF MANGANESE.

To the Editor of the Chemical News.

SIR,—Mr. Ramage's conclusion "that the rare metals now used in the manufacture of certain special steels do not interfere when present only in small quantities," hardly does justice to the account we gave of the influence of these metals when present in such amounts as the Sheffield steel manufacturers think it desirable to introduce. We said nothing about their being present only in small quantities; in fact, in their alloys they are neces-

sarily present in large quantities, and both then and otherwise some of them *do* interfere with the manganese estimation, if the final titration is made with hydrogen peroxide.

It is true that the only point dealt with in our private correspondence with Mr. Ramage was whether the correct result was obtained by filtering the permanganate into hydrogen peroxide or by filtering into an empty flask. The correspondence originated by our communicating the observation that when the permanganate was filtered into peroxide, the results obtained were higher than when it was filtered into an empty flask and peroxide added afterwards. Mr. Ramage's criticism of our paper compels us to state that he at first refused to credit this, and assured us that he preferred the same mode of working for steels as for spiegels, &c., and practised it. We are sorry to remind him of this, as well as of the fact that some time later he admitted the difference, and, as he says, sent one of us a report which purported to explain it.

We are surprised to find that Mr. Ramage refers to this report at all, because it failed hopelessly to elucidate the cause of the differing results. Mr. Ramage had maintained, and the report alluded to attempted to prove—by comparison of results with what we suppose were absolute standards and otherwise—that it was correct to filter into an excess of hydrogen peroxide. On the contrary, we were experimentally satisfied that it was better to filter into an empty flask. Mr. Ramage's first paper justified our position by advocating this procedure.

We do not contend that the *intended* point of the footnote in the *Trans. Chem. Soc.*, 1895, 275, was well hit off by our reference to it, but the matter of fact of the footnote, which so largely influences Reddrop and Ramage's deductions in their Chemical Society's paper, was nevertheless truly represented. They say in effect that the nitric acid solution of ferric nitrate decomposes permanganate more readily than it does hydrogen peroxide, and they argue from this that "all the results obtained by Schneider's method will be below the truth," because Schneider filters into an empty flask instead of into an excess of peroxide as they do in the assay of rich manganese alloys. Now, in Mr. Ramage's paper (Chemical News, vol. lxxxiv., p. 209), he admits that for each c.c. of decinormal hydrogen peroxide added to a solution containing 1·1 grms. of steel or iron in nitric acid, about 0·1 c.c. is at once reduced; that is to say, the hydrogen peroxide is decomposed by the ferric nitrate much more readily and extensively than permanganate could be, which is certainly contrary to the statement of the footnote referred to.

No question of inaccuracy has, as Mr. Ramage says (Chemical News, lxxxiv., 209), been raised regarding the results obtained in the analysis of ferromanganese and spiegel. But unless he can show that the reaction between acid solutions of ferric nitrate and hydrogen peroxide ceases when several times less than 1·1 grms. of iron and much manganese are present, the said question of inaccuracy certainly ought to be raised and settled. For it appears to us at any rate possible, that the 0·6 per cent difference which was found by Reddrop and Ramage between the results of assays of an 80 per cent ferromanganese by their mode of procedure and Schneider's, may actually measure the deficiencies of their mode and not those of Schneider's.

The rest of our differences with Mr. Ramage are either matters of opinion which do not materially interfere with the working of the process either way, or they are such points as interested persons may settle for themselves by a few simple experiments.

We adhere most strongly to ferrous ammonium sulphate in preference to hydrogen peroxide. We quoted no test analyses in support of this modification because we consider them to be unnecessary. But for a considerable time an abundance of tests has been accumulated from at least a dozen sources; we will oblige Mr. Ramage with one of many similar series of determinations as evidence of our desire to ascertain the truth.

Mode of estimating the manganese.	Resulting percentage Mn. I. Carbon, 1·12 per cent.	II. Carbon, 0·34 per cent.	III. Carbon, 2·25 per cent.
1. Gravimetric estimation of the Mn	0·32	1·03	0·92
2. Bismuthate — Filtration into empty flask	0·32	1·00	0·84
3. Bismuthate—Filtration into excess H_2O_2..	0·36	1·10	0·95
4. Organic matter destroyed in hot solution with bismuthate, filtration into empty flask, and titration with ferrous sulphate ..	0·31	1·01	0·89
5. As in 4—Filtration into excess ferrous sulphate	0·30	1·01	0·88
6. Acetate separation of iron—Filtrate precipitated with Br and AmHO. Precipitate ignited, dissolved in HCl, evaporated with H_2SO_4, and finished by oxidation with bismuthate and titration with H_2O_2.. ..	0·32	1·02	0·90

—We are, &c.,

Fred. Ibbotson.
Harry Brearley.

Bower Road, Sheffield.

THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

Sir,—If, as a consequence of the voting upon Professor Frankland's motion at last Thursday's Extraordinary General Meeting of the Chemical Society, the day and hour of meeting of the Society are to be changed to 5.30 p. m. on Wednesday, as arranged by the Council, it will be most unfortunate for all who are in positions similar to ours; and they are not a few, and are rapidly increasing in number.

We are engaged in research work of a technical character in a factory some 10 miles from Burlington House, and as our working day is not done till 6 o'clock we cannot possibly attend a meeting at 5.30 p.m.; indeed, it has always been as much as we could manage conveniently to be there by 8 o'clock.

We have, however, been regular attendants; one of us for over four years.

Mr. Howard stated at Thursday's meeting that it would be more convenient for him and his brothers to have the hour changed to 5.30 p.m., and that every facility would be given to their chemists to attend at that hour. But, in the first place, Mr. Howard's attitude is not at all representative of the views taken by employers, many of whom are not chemists, and do not appreciate the necessity for keeping in touch with modern thought; and, secondly, a chemist worth his salt and engaged in research work does not wish to leave his work untouched for an afternoon every fortnight, nor would he do so even if his employer gave consent.

We wish to emphasise the fact that there is a growing number of chemists, working in or near London, who are in the position of having, more or less, to justify their appointment by producing results, and effecting improvements in commercial processes.

These men want and deserve encouragement, and do not wish to be denied those privileges of discussing problems and getting new ideas which they have hitherto enjoyed through the Chemical Society. They will not leave their work to attend meetings at 5.30 p.m. except very occasionally.

It is admitted by all parties that the expression of opinion by the Fellows, per the original postcard, is not what would be given now that the position is more clearly understood. Further, it is obvious, and was admitted by

Professor Smithells on Thursday, that the country members are, with rare exceptions, quite indifferent to the day and hour of meeting; they would not come in appreciably larger numbers than they do, no matter when the meetings were held.

At the same time there could be, we imagine, no objection on the part of the London Fellows to an occasional meeting at 5.30 p.m., as Professor Ramsay suggested, for the sake of the Country Fellows, if they so desired; and no doubt the London Fellows would make special efforts to attend on such occasions in order to meet old friends.

We desire, in conclusion, to express our thanks to those gentlemen who have done so much to represent the position in this matter of that class of chemists to which we belong.—We are, &c.,

TWO FACTORY RESEARCH CHEMISTS.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 22, November 25, 1901.

Compounds of Aluminium Chloride with the Alkaline Chlorides.—E. Baud.—Amongst the spinel chlorine compounds are found the following mixed chlorides:—$Al_2Cl_6.3NaCl$ and $Al_2Cl_6.3KCl$; also, very probably, the chlorated cryoliths $Al_2Cl_6.6NaCl$ and $Al_2Cl_6.6KCl$. Even these latter bodies do not apparently represent the limiting compounds of Al_2Cl_6 with the alkaline chlorides, but it is difficult to establish thermometrically the existence and the exact composition of the higher ones, on account of the very small proportion of heat evolved during the fixation of the last molecules of the alkaline chlorides.

Preparation of Barium.—M. Guntz.—Pure barium has never been obtained up to the present time. The author finds, however, that, during certain experiments on the stability of barium amalgam, he obtains the metal in a pure state and is able to study its properties. The barium amalgam is obtained very easily and in considerable quantity by the electrolysis of a saturated solution of $BaCl_2$, the cathode being made of mercury and the anode of an alloy of platinum and iridium. A 3 per cent amalgam of barium is obtained, from which the barium is prepared by distilling off the mercury in a vacuum at a bright red heat. Barium in a metallic state is a silver white metal, as soft as lead. It fuses at a dull red heat, and is very volatile at bright red heat. It rapidly oxidises in the air, giving baryta in the form of a condensed powder.

A New Volatile Salt of Beryllium.—G. Urbain and H. Lacombe.—When beryllium hydrate is dissolved in dilute acetic acid and the whole evaporated over the water-bath, a gummy mass is obtained; this substance presents none of the characteristics of a definite compound. If, however, this mass is treated with crystalline acetic acid at boiling-point, a solution is obtained which, on cooling, deposits first needle-shaped crystals, and, at a lower temperature, small octahedral crystals. The molecular weight and analysis of this crystalline compound show it to have the formula $[CH_2CO_2]_6Be_4O=406$, admitting $Be = 9$ and $BeO = 25$. It is impossible to reconcile the composition of the body and density of the body by supposing $Be=13{\cdot}5$ and $Be_2O_3=77$. This new compound affords, therefore, a new argument in favour of the diatomicity of beryllium. The authors are continuing their researches on this subject.

Action of Fuming Sulphuric Acid on Ethylic and Propylic Aldehydes and Acetone.—Marcel Delépine.—The author's researches on the action of fuming sulphuric acid on ethylic and propylic aldehydes and acetone show that these aldehydes and acetone, which are acted upon by ordinary strong sulphuric acid, react in a more definite manner with the fuming acid. In fact, these compounds fix a certain number of molecules of SO_3, giving rise to stable salts of the acid when in acid or neutral media, but salts which are very easily changed by alkalis; these latter breaking the carbon chain in two places.

Electrolytic Preparation of the Halogen Compounds of Acetones.—A. Richard.—If an electric current traverses a mixture of hydrochloric acid and acetone, at the end of an indefinite period a dark liquid is obtained which attacks the eyes; this liquid is monochloracetone, $CH_2-CO-CH_2Cl$. An analogous reaction occurs if an electric current passes through a mixture of hydrobromic acid and acetone. In this case it is monobromacetone, $CH_3-CO-CH_2Br$, which is produced. These two reactions have been noticed by several chemists, but have not been the object of systematic research. The author therefore undertakes this investigation, examining the conditions of preparation, purification, and principal reactions of the two halogen acetones.

Transformation of two Xanthydrols into Xanthenes by a New Reaction.—R. Fosse.—The author's researches were carried out on dinaphthoxanthydrol and xanthydrol; his experiments on their transformation into xantheoses lead him to the following conclusions:—1. The monohalogen derivatives of the xanthene series obtained either by the action of the halogens on the xanthenes or by the action of the fuming hydracids on the xanthydrols behave as basic salts and give double salts with several alkaloid reagents. (2). These same bodies react on alcohol in the same manner as diazoic salts; they form the corresponding carbide, transforming alcohol into aldehyde and giving the hydracid.

Etherification of Phosphorous Acid by Glycerin and Glycol.—P. Carré.—If equimolecular proportions of glycerin and phosphorous acid are heated together, a certain proportion of the acid is etherified—the proportion varying with the conditions of the experiment. From the actions of the phosphoric acid on litmus solution and phenolphthalein, the author concludes that the reaction takes place according to the equation—

$$P(OH)_3+CH_2OH-CHOH-CH_2OH = \begin{matrix} O \\ H \end{matrix}\!\!>\!P-O-CH_2-CHOH-CH_2OH+H_2O,$$

and that the glycerophosphorous acid formed is monobasic to litmus and to phenolphthalein. This property enables him to estimate the etherification by simple volumetric titrations. The reaction of glycol is comparable with that of glycerin, furnishing the acid,—

$$\begin{matrix} O \\ H \end{matrix}\!\!>\!P-O-CH_2-CH_2OH.$$

The barium salt of this acid is also prepared; its formula, $P_2O_3H_{12}C_4Ba$, being established by analysis.

MEETINGS FOR THE WEEK.

SATURDAY, 28th.—Royal Institution, 3. (Christmas Lectures to Young People). "On Waves and Ripples in in Water, Air, and Æther," by Professor J. A. Fleming, M.A., F.R.S., D.Sc.

ST. PAUL'S SCHOOL.—An Examination will be held at St. Paul's School, West Kensington, on Tuesday, January 14th, 1902, and following days, for filling up about Four Vacancies on the Foundation.—Full particulars can be obtained from the Bursar.

THE CHEMICAL NEWS.

Vol. LXXXIV., No. 2196.

ON THE

MUTUAL ACTION OF ALUMINA AND FERRIC OXIDE AT INCIPIENT WHITE HEAT.

By H. WARTH, D.Sc.
Late Deputy Superintendent Geological Survey of India.

During an examination of gibbsite ($Al_2O_3,3H_2O$) from the Madras Presidency, possessing a pale reddish colour due to ferric oxide, I was much struck by the manner in which the mineral turned perfectly white when heated over the blowpipe flame, and decided to inquire into the cause of the phenomenon.

The decoloration in question is mentioned by Dana, who suggests, however, no explanation of it.

One of the first experiments I made was the following:—Ammonia was added to a solution containing aluminic and ferric salt in such proportion that the precipitate, after expelling the water, contained exactly 1 per cent. of Fe_2O_3. This mixed precipitate, after heating over a Bunsen flame, was much less coloured than the gibbsite just alluded to, and on heating it over the blowpipe flame it became pure white. I now treated this white product after pulverisation with ferric salt and ammonia in such a way that it became coated, as it were, with ferric oxide, the latter amounting to 0·5 per cent of the whole, and after heating gently over the Bunsen flame it had imparted a good red colouring very similar to that of the natural gibbsite, only stronger. I estimated the depth of tint as equal to three units of colour, a unit having been arbitrarily chosen in the shape of a rather red sample of gibbsite. Heating this powder, which had 3 units of colour, over the blowpipe flame rendered it snow white. A second treatment, adding 1 per cent more Fe_2O_3, had a similar effect, leaving the sample containing in the aggregate 2·5 per cent Fe_2O_3, with a brownish white tint equal by guess to 0·1 of my assumed unit of colour.

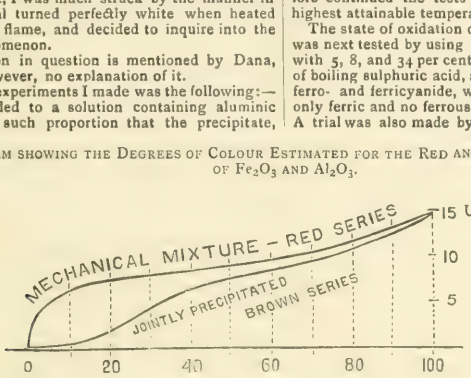
It was thus proved that alumina had the property of nearly completely decolorising red oxide of iron at the temperature of the blowpipe flame, and there remained no doubt that the gibbsite owes its decoloration before the blowpipe to this property of the alumina. I also added some pure dry ferric oxide to some whitened gibbsite in the proportion of 1 per cent, which made the sample pink, say about 2 units, and on heating over the blowpipe flame, this colour almost entirely disappeared, thus again showing that the dry substances react by a kind of cementation process at the temperature of the blowpipe flame.

In the next step of this enquiry I gradually increased the proportion of ferric oxide in the mixed precipitate, and I found the decoloration to continue up to 7 per cent Fe_2O_3, but beyond this there was a slowly increasing brown tint, which was well pronounced when 18 per cent of Fe_2O_3 had been reached. This brown colour continued to 34 per cent Fe_2O_3 without any admixture of red. Beyond this at 60 per cent and 75 per cent there was a darker brown with perhaps a tinge of red, but it was clear that throughout I had to deal with a series of various shades of brown. I have attempted to represent the series by a diagram, but I would mention that this diagram is merely based on ocular estimation.

The ignition was at first effected in a platinum crucible, but thin layers of the mixtures in contact with the walls of the crucible were sometimes altered, probably owing to the passage of hydrogen through the platinum. I therefore continued the tests in a porcelain crucible at the highest attainable temperatures.

The state of oxidation of the iron in the ignited samples was next tested by using for this purpose the precipitates with 5, 8, and 34 per cent of Fe_2O_3. I dissolved by means of boiling sulphuric acid, and added solutions of potassium ferro- and ferricyanide, which proved unmistakeably that only ferric and no ferrous oxide was present in all cases. A trial was also made by that delicate magnetic method of weighing with and without magnet beneath the pan which General McMahon has introduced, which showed the absence of magnetic oxide (Fe_3O_4), so that we clearly have to do with a combination of Al_2O_3 and Fe_2O_3 only.

Diagram showing the Degrees of Colour Estimated for the Red and Brown Mixtures of Fe_2O_3 and Al_2O_3.



All the above-mentioned mixtures of simultaneously precipitated Fe_2O_3 and Al_2O_3 which had been ignited over the blowpipe flame were of a brownish tint, and quite different in colour from an unignited mixture of pure anhydrous Fe_2O_3 and pure anhydrous Al_2O_3. The latter mechanical mixtures are all red and the amount of tint is shown by a curve in the above-mentioned diagram. The red series shows a rapidly rising curve. The two curves (for the red and the brown series), are widely divergent when the percentages of Fe_2O_3 are low; the one is convex while the other is concave. The colouring of the red series is very strong in comparison with that of the brown series. There is undeniable decolorisation in the case of the latter.

This behaviour of alumina with ferric oxide may be compared with the well-known cobalt-nitrate blowpipe test. The beautiful colour obtained in the latter reaction may also be produced from the solid oxides without the application of any solvent, and it seems that some kind of cementation of the solid substances takes place at the temperature of the blowpipe flame. Fresenius ("Qualitative Analysis," 10th ed., p. 105), says the blue substance is "a compound of the two oxides."

As already mentioned, dry ferric oxide mechanically mixed with alumina in the proportion of 1 per cent likewise became decolorised at the temperature of the blowpipe flame. This experiment was subsequently repeated

with larger proportions, and with some care a mixture containing as much as 34 per cent of red ferric oxide acquired a brown tint very similar to the 34 per cent sample of the brown series obtained from the jointly precipitated oxides.

It is a remarkable circumstance that ferric oxide by itself has at the temperature of the blowpipe flame already a decided tendency to change into magnetic oxide (which it does entirely at a full white heat), and that this tendency is checked by the presence of alumina, as is undoubtedly demonstrated by the above experiments.

But more than this, a mixture of alumina with 6·8 per cent of finely pulverised magnetic oxide (Fe_3O_4) after careful ignition also acquired a brown tint, and was finally found free from ferrous oxide, the iron being entirely ferric. The contact with alumina at the temperature of the blowpipe flame had thus induced the Fe_3O_4 to take up more oxygen and to be changed into Fe_2O_3. The above experiments thus seem to indicate that the molecules of iron are enabled by the presence of alumina to combine with a larger proportion of oxygen than if left to themselves.

As regards the change of colour of the mixtures from red to brown, this need not imply a chemical combination between the Fe_2O_3 and Al_2O_3. We are familiar enough with changes of colour when differently coloured metals form, for instance, alloys such as brass, and it appears also possible that two oxides which are so decidedly isomorphous as Fe_2O_2 and Al_2O_3 may diffuse into each other with change of colour without their forming a compound.

VOLUMETRIC DETERMINATION OF ALUMINA FOR TECHNICAL PURPOSES.

By C. R. GYZANDER.

(Concluded from p. 297).

Determination of Basic Alumina.

To 50 c.c. each of the alum solutions before mentioned were added 0·6 c.c. standard soda solution, equivalent to 0·6 per cent Al_2O_3.

Two c.c. standard sulphuric acid were next added, and the whole left standing, with occasional stirring, to dissolve the hydrate of alumina thrown out. Two drops methyl indicator and 100 c.c. distilled water were then added and standard soda solution run in, drop by drop and with constant stirring for a few seconds between each drop, until the colour changed to orange. The number of cubic centimetres of standard soda solution used were subtracted from 2, and the remainder expressed per cent basic alumina found. The following results are the average of five determinations:—

	NaOH consumed.	Basic Al_2O_3 found.	Error.
	C.c.	Per cent.	
1.	1·4	0·6	0·0
2.	1·4	0·6	0·0
3.	1·4	0·6	0·0
4.	1·4	0·6	0·0
5.	1·4	0·6	0·0
6.	1·5	0·5	− 0·1
7.	1·8	0·2	− 0·4
8.	2·0	0·0	− 0·6
9.	2·1	0·0	0·0

These results show that the basic alumina was correctly determined in sulphates containing up to 60 per cent $Al_2(SO_4)_3$. Above that percentage, the orange point is no longer the correct end-point for neutrality, as this begins to turn more and more towards the red-orange with increase of $Al_2(SO_4)_3$. It appears from these tests as if No. 8 was neutral and No. 9 acid, equivalent to 0·1 c.c. standard soda solution, which would be 0·29 per cent H_2SO_4.

The basic alumina is, however, easily determined, even in such high testing sulphates, if the point of neutrality is compared with a blank made from pure alum and containing the same percentage of $Al_2(SO_4)_3$ as the sulphate to be tested. Thus, 50 c.c. each of the alum solutions —from No. 6 to No. 9 inclusive—were treated with 2 drops of methyl indicator and 100 c.c. distilled water, and these served as blank standards with which the titration end-points were compared in another 50 c.c., made basic by the addition of standard soda solution, and the results were in every instance correct.

In testing for total $Al_2(SO_4)_3$, it is not immaterial whether the sulphate is originally basic or neutral; because, if the sulphate is basic, and this is not corrected by adding sulphuric acid, then the results will be much too low, as basic salts are thrown down by the caustic solution, whether this be strong or dilute, as the following test will show.

16·6066 grms. of alum were dissolved in about 500 c.c. distilled water, and then made basic by adding 20 c.c. standard soda solution. The alumina at first thrown out dissolved completely upon shaking; the solution was made up to a litre. We have here a solution equivalent to sulphate containing 56·67 per cent $Al_2(SO_4)_3$, with 1·0 per cent basic.

Fifty c.c. of this solution, 2 drops methyl, 4 drops phenol indicator, and 100 c.c. distilled water gave, on an average of five determinations, 16·64 per cent Al_2O_3 or 55·41 per cent $Al_2(SO_4)_3$, a difference of 1·26 per cent. This is a much greater difference than resulted in testing a 60 per cent neutral sulphate (see No. 5). The dilute standard gave 55·92 per cent $Al_2(SO_4)_3$, a difference of 0·75 per cent.

To another 50 c.c. were added 2 c.c. standard sulphuric acid, then indicators and distilled water as before. Standard soda required to orange was 1 c.c., or basic Al_2O_3 is 1 per cent. Continuing the addition of standard soda to permanent pink required, on an average of five determinations, 18·94 c.c. Deducting from these, 2 c.c. acid originally added, leaves 16·94 per cent Al_2O_3 or 56·41 per cent $Al_2(SO_4)_3$, which result is practically correct. In like manner, when using dilute standard soda solution, there was required, on an average of five determinations, 63·16 c.c. Deducting the equivalent of 2 c.c. standard acid, or 6·6 c.c. dilute standard, leaves, as final result, 56·56 per cent $Al_2(SO_4)_3$.

The influence of temperature on the determination of alumina will be seen from the following. Fifty c.c. alum solution, containing the equivalent of 10 grms. of a 58 per cent sulphate per litre (see No. 4 in table) gave at—

°C.	Per cent Al_2O_3.
25	17·4
30	17·5
35	17·8
40	18·3
45	18·7
50	19·3

When another 50 c.c. of the same solution, and indicators as before, were heated to 50° C., and 18·5 c.c. of standard soda added, the colour was yellow, due to the methyl-orange, but showed no trace of pink, although 1·06 c.c. excess of alkali had been added. As the solution gradually cooled, the pink colour began to appear, and at 35° C. the colour was intensely red, which shows that alumina is acid to phenolphthalein at high temperatures.

Determination of Free Acid in Sulphate of Alumina.

It has already been mentioned that an increase in $Al_2(SO_4)_3$ alters the colour produced by methyl-orange, and the more concentrated the solution is, the more noticeable is this colour change. As commercial sulphates vary from 50 to 58 per cent, the amount of sulphate contained in half a grm. would vary from 0·25 to 0·29 grm. Potash alum containing equivalent quantities of sulphate of alumina would then be 0·6919 and 0·8026 grm.

These quantities were dissolved in 150 c.c. water and 2 drops of methyl indicator added. Comparing the shades produced with that of 0·5 grm. alum in 150 c.c. distilled water and 2 drops methyl indicator, there was a barely perceptible difference between them; that is, one might have called the one containing 0·5 grm. of alum for orange and the others red-orange, but for all practical purposes they were alike. By adding tenth-normal sulphuric acid to the alum solution containing 0·5 grm. in 150 c.c., it was found that 0·2 c.c. gave a barely perceptible red-orange, 0·4 c.c. a distinct red orange, while 1 c.c. was strongly pink coloured. Referring the amount of sulphuric acid added to 0·5 grm. original alum, we find that about 0·2 per cent free acid would be detected with difficulty, while twice the amount or more is readily detected by comparing the colour produced with methyl-orange with that of 0·5 grm. alum in 150 c.c. water. If, therefore, a sulphate, when tested as already described for basic, consumes more than 2 c.c. standard soda to neutral, then the excess must be due to free sulphuric acid in the sulphate. When the excess of standard soda solution required to produce the neutral tint is more than 0·2 c.c., the acidity must already have made itself noticeable by the pink colour produced with the methyl indicator, but when the excess of standard soda required to neutral is trifling, or when the results indicate neutrality, there may be a doubt as to the actual acidity or neutrality of the sulphate, as small differences may be due to experimental errors. For practical purposes, such small differences may be neglected, although there occasionally are cases where it is desirable to be able to say with certainty whether a sulphate is actually normal or not.

An attempt to determine free acid in sulphate of alumina by means of alcohol, whether anhydrous or not, was an absolute failure, as a dissociation of the alum always takes place, whereby free acid and basic salts are formed. The following method, based on the behaviour of sulphate of alumina towards ultramarine, was found to give perfectly satisfactory results. As ultramarines differ in their sensitiveness toward acid, the brand that is the most sensitive will be the best for this test. The one I used was known as "E No. 1" of Heller and Merz Co. of New York. I first made up the following solutions:—

Grms.	C.c.	Per cent.
1. 10 of alum	+ 2 N/10 H_2SO_4	= 0·1 free H_2SO_4
2. 10 ,,	+ 1 ,, ,,	= 0·05 ,, ,,
3. 10 ,,		= neutral
4. 10 ,,	+ 1 standard soda	= 0·05 basic alumina
5. 10 ,,	+ 2 ,, ,,	= 0·1 ,, ,,

Each was made up to 100 c.c.

0·5 grm. ultramarine were shaken up with 500 c.c. distilled water.

Five small flasks containing 20 c.c. of the above alum solutions (2 grms. original alum) and 10 c.c. ultramarine solution = 0·01 grm., were placed on a hot radiator and each stirred up by gently rotating the flask; this was kept up until no more blue colour was visible when holding the flask against a white paper.

No. 1 was colourless	in	4·5	minutes
,, 2 ,,	,,	6·5	,,
,, 3 ,,	,,	8·5	,,
,, 4 ,,	,,	9·0	,,
,, 5 ,,	,,	9·5	,,

Repetition of the experiment gave practically the same results, as the following figures show:—

No. 1 was colourless	in	5	minutes
,, 2 ,,	,,	7	,,
,, 3 ,,	,,	8	,,
,, 4 ,,	,,	9	,,
,, 5 ,,	,,	9·5	,,

In these two series of tests the ultramarine was added to No. 1 solution first, and then in succession, in numerical order. Although the measuring of the ultramarine with a pipette was quite rapid, yet some little time elapsed between the first and last addition, and as this might possibly have some influence on the earlier loss of colour in the first samples, the test was repeated, but the order of adding the ultramarine was reversed, so that it was added to No. 5 first and to No. 1 last. The results were as follows:—

No. 1 was colourless	in	5	minutes
,, 2 ,,	,,	7	,,
,, 3 ,,	,,	8	,,
,, 4 ,,	,,	10	,,
,, 5 ,,	,,	10·5	,,

The order of adding the ultramarine had therefore no influence on the results. It is also seen that an increase of acidity of the sulphate of alumina from 0·05 to 0·1 per cent had a marked influence on the decomposition of the ultramarine as compared with normal sulphate. It also shows that an increase of basic alumina, even though only from 0·05 to 0·1 per cent, diminishes the action upon the ultramarine, and that the difference in action between 0·05 per cent free acid and 0·05 per cent basic alumina is very marked. Such small amounts of free acid and basic alumina cannot be detected by titration, but are readily detected by the ultramarine method. In carrying out the test on a doubtful sulphate proceed as follows:—Weigh pure potash alum equivalent to the $Al_2(SO_4)_3$ in 2 grms. of the sulphate in question in several portions, and make them of known acidity and basicity by adding N/10 acid, and standard soda solution. Weigh also 2 grms. of the sulphate in question, and dissolve them each in 20 c.c. distilled water. Add 10 c.c. ultramarine solution, place on a warm radiator, and note the time each requires to be decolorised. The sample decolorised in the same time as the sulphate in question must be equal to it in composition. A certain sample of sulphate of alumina was found to have the following composition when tested gravimetrically:—

Al_2O_3	=	16·750
SO_3	=	39·241
FeO	=	0·021
SiO_2	=	0·009
Insoluble ..	=	0·430
Na_2O	=	0·049
H_2O	=	43·500 (by difference)
		100·000

The above is calculated as:—

$Al_2(SO_4)_3$	=	55·780
Free H_2SO_4	=	0·153
$FeSO_4$	=	0·044
SiO_2	=	0·009
Insoluble	=	0·430
Na_2SO_4	=	0·112
H_2O	=	43·472
		100·000

Tested volumetrically as described the following results were obtained:—

$Al_2(SO_4)_3$	=	55·810
Free H_2SO_4	=	0·200
$FeSO_4$	=	0·044
Insoluble	=	0·430
H_2O, &c.	=	43·516
		100·000

Another chemist tested this same sulphate, and reported 0·4 per cent basic alumina. At the same time he stated

that he had used Beilstein and Grosset's method for determining free acid in alum, and had by that method found 0·25 per cent free acid. This result was, however, rejected, as the gravimetric method was considered to be the correct thing.

Starting from my own determination, 55·81 per cent $Al_2(SO_4)_3$, 2 grms. of the sulphate is equivalent to 3·0893 grms. potash alum. If this is made 0·4 per cent basic it would require 2·5 c.c. standard soda solution. But the addition of this amount of standard soda would precipitate alumina equivalent to 0·1151 grm. alum. Alum equivalent to 55·81 per cent $Al_2(SO_4)_3$, and made 0·4 per cent basic by addition of standard soda solution, would therefore be 3·0893 + 0·1151 = 3·2044 grms.

The following five solutions were made :—

Grms.		C.c.		Per cent.
1. 3·0893 alum	+	0·6 N/10 H_2SO_4	=	0·1 free acid
2. " "	+	0·3 "	=	0·05 "
3. " "		—	=	neutral
4. " "	+	2·5 standard soda	=	0·4 basic Al_2O_3
5. 2 grms. of the sulphate in question.				

Each was dissolved in 20 c.c. distilled water in an Erlenmeyer flask by the aid of heat, and then cooled down to room temperature; 10 c.c. of the well-shaken ultramarine solution added, and the test carried out as already described.

No. 1 was decolorised in 4 minutes
" 2 " " " 5 "
" 3 " " " 6 "
" 4 " " " 13 "
" 5 " " " 2 "

As No. 5, or the sulphate in question, was the first to be decolorised, it is evident that it must be more acid than No. 1, which was the next to be decolorised, and could not possibly have been 0·4 per cent basic, as the sulphate No. 4, which had that composition, required thirteen minutes for the decomposition of the ultramarine.

Analysis of Bauxite Sulphate.

As both ferric and ferrous sulphate may be accurately determined in exactly the same manner as alumina, provided they are not present in too large amounts, in which case the end-point is obscured by the strongly coloured precipitate formed, all that is needed is to correct for iron in the results of total sulphates when the remainder is alumina. Proceed, therefore, exactly as stated for hydrate sulphate, but determine the total and ferrous iron in two separate portions of 100 c.c. each, strongly acidified with sulphuric acid. For total iron, add liquid sulphurous acid to reduce any ferric iron to the ferrous state, boil off the excess of SO_2, cool, and titrate with dilute permanganate solution. Ferrous iron is obtained by titrating the other 100 c.c. direct. Subtracting the ferrous from total iron gives the equivalent of ferric iron. The only precaution needed is to have the permanganate solution dilute, titrate in the cold, and to take the first faint pink colour, lasting about a second, as end-point. The pink colour usually disappears after a little while, due to humus compounds which all Bauxite sulphates contain in varying quantities, or possibly to arsenious acid occasionally also present. These two compounds decompose permanganate only very slowly in the cold, and do therefore not occasion any very great error in the results of the iron determination for technical purposes. The iron is calculated as $FeSO_4$ or $Fe_2(SO_4)_3$, as the case may be, and its equivalent of standard soda solution, with reference to 0·5 grm. as well as the basic alumina, deducted from the total alumina found, when the remainder, times 3·33, gives $Al_2(SO_4)_3$. The permanganate solution which I use requires 30 c.c. for 0·7 grm. ferrous-ammonium sulphate. The following table shows its equivalent of ferrous and ferric sulphate as well as standard soda solution :—

C.c. Permanganate.	Per cent. $FeSO_4$.	NaOH. Correction.	Per cent. $Fe_2(SO_4)_3$.	NaOH. Correction.
0·1	0·08	0·019	0·11	0 034
0·2	0·17	0·038	0·22	0·068
0·3	0·25	0·057	0·33	0·102
0·4	0·34	0·076	0·44	0·136
0·5	0·42	0·095	0·56	0 170
0·6	0·51	0 114	0·67	0·204
0·7	0·59	0·133	0·78	0·238
0·8	0·68	0·152	0·89	0·272
0·9	0·76	0·171	1·00	0·306
1·0	0·85	0·190	1·11	0·340
1·1	0·93	0·209	1·22	0·374
1·2	1·02	0 228	1·33	0·408

15·7757 grms. alum were dissolved in 500 c.c. distilled water, and 12 c.c. standard soda solution added. When clear, 0·1828 grm. pure $FeSO_4$+7aq. was added, and the whole made up to 1 litre. This gives a solution equivalent to 10 grms. of a sulphate of the following composition :—

	Per cent.
$Al_2(SO_4)_3$	55·00
Basic alumina	0·60
$FeSO_4$	1·00
Water, &c.	43·40
	100·00

Fifty c.c. of this solution, 2 c.c. standard acid, 2 drops methyl indicator, 4 drops phenol indicator, and 100 c.c. distilled water gave for basic alumina 0·7, 0·6, 0·6, 0·5; average, 0·6 per cent. Total sulphates obtained were 17·3, 17·4, 17·4, 17·4, 17·4; average, 17·38.

One hundred c.c. acidified with sulphuric acid required for ferrous iron 1·2 c.c. permanganate solution, or 1·02 per cent $FeSO_4$. 100 c.c. of the solution, strongly acidified with sulphuric acid, 10 c.c. of a 6 per cent SO_2 solution added, the excess of SO_2 boiled off, the solution cooled, and titrated with permanganate, required for total iron 1·2 c.c. as before. There was, therefore, no ferric iron present.

1·02 per cent $FeSO_4$ corresponds to 0·228 c.c. standard soda solution. Adding this to the 0·6 per cent basic gives a total correction 0·828, which subtracted from 17·38 leaves as remainder 16·552, which multiplied by 3·33 gives 55·12 per cent $Al_2(SO_4)_3$. The results were therefore :—

$Al_2(SO_4)_3$	55·12
Basic Al_2O_3	0 60
$FeSO_4$	1·02
Water, &c.	43·26
	100·00

which results are satisfactory.

A commercial Bauxite sulphate gave the following result by gravimetric method :—Insoluble = 0·06, SiO_2 = 0·01, As_2O_5 = 0·03, FeO = 0·04, Fe_2O_3 = 0·27, Al_2O_3 = 17·76, CuO = 0·003, Na_2O = 0·19, H_2O = 41·44, SO_2 = 40·37; total, 100·143 per cent. These results are equivalent to :—

$Al_2(SO_4)_3$	56·687
Basic Al_2O_3	0·74
$FeSO_4$	0·08
$Fe_2(SO_4)_3$	0·67
$CuSO_4$	0·006
Na_2SO_4	0·42
SiO_2	0·01
As_2O_5	0·03
Insoluble	0·06
H_2O	41·44
	100·143

The volumetric determination gave the following result :—Basic alumina 0·85, 0·85, 0·85. Total sulphate 17·95, 17·95, 17·90; average, 17·93.

$FeSO_4$ .. = 0·08 per cent = 0·019 NaOH correction
$Fe_2(SO_4)_3$ .. = 0·67 per cent = 0·204 NaOH correction
0·85 basic

1·073 total correction
$(17·93 - 1·073) \times 3·33 = 56·13$ per cent $Al_2(SO_4)_3$.

Total results :—

$Al_2(SO_4)_3$	56·13
Basic alumina	0·85
$FeSO_4$	0·08
$Fe_2(SO)_3$	0·67
Insoluble	0·06
Water, &c.	42·21
	100·00

Analysis of Sulphate of Alumina containing Zinc Sulphate.

The sulphuric acid in zinc sulphate cannot, like that in sulphate of iron and alumina, be titrated with standard soda solution in the cold. If the solution, containing only zinc sulphate, is boiling hot, then the results are correct when phenolphthalein is indicator. As sulphate of alumina cannot be tested under these conditions, it follows that a separation of the two is necessary before they can be determined. Zinc can be separated from alumina by means of H_2S in a solution slightly acidified with H_2SO_4, and the ZnS thrown down filters readily if the precipitation is started in a hot solution and continued until cold. The filtered and washed ZnS, after being converted into sulphate or chloride, may be titrated with standard soda solution at a boiling temperature. But another and quicker method is the following :—

When H_2S is led into a solution of $ZnSO_4$, the following reaction takes place: $ZnSO_4 + H_2S = ZnS + H_2SO_4$. For every molecule of ZnS formed one molecule of H_2SO_4 is liberated. If, therefore, the free acid formed is determined, the zinc may be calculated from it.

One c.c. standard soda solution is equivalent to 0·02344 grm. $ZnSO_4$.

Ferric sulphate also liberates sulphuric acid when reduced to ferrous sulphate ; thus :—

$$Fe_2(SO_4)_3 + H_2S = 2FeSO_4 + H_2SO_4 + S.$$

Basic alumina, if present, will neutralise an equivalent amount of acid, all of which must be borne in mind. The analytical operation will, therefore, be as follows :—Dissolve 10 grms. in distilled water, and filter. Dilute to 1 litre, and mix by shaking. In 50 c.c. determine basic Al_2O_3, and in 100 c.c. each, ferrous and ferric sulphates. To other 50 c.c. add standard sulphuric acid, equivalent to basic alumina present ; heat to near boiling, and pass H_2S through until cold. Allow to settle, and filter the solution. If for any reason the solution does not filter clear, return the filtrate until it is clear, then wash the precipitate thoroughly with distilled water containing a little H_2S. Boil the clear filtrate to expel H_2S, and bring the volume down to 150 c.c. if need be. Cool, and determine free acid, after adding 2 drops of methyl indicator, by titration with standard soda solution to orange, then add 4 drops of phenol indicator, and titrate as mentioned for total sulphates, which now includes all the iron as $FeSO_4$. From the total sulphates found, deduct the standard soda equivalent of total iron as $FeSO_4$ + basic, and the remainder, times 3·33, is $Al_2(SO_4)_3$. From the free acid found after precipitation with H_2S, deduct that equivalent to $Fe_2(SO_4)_3$ (the basic was corrected for by adding standard acid before H_2S treatment), and the remainder is calculated as $ZnSO_4$.

An artificial aluminium-zinc sulphate was prepared as follows :—15·7757 grms. pure potash alum were dissolved in 500 c.c. distilled water, and 12 c.c. standard soda added. When clear 0·1828 grm. $FeSO_4$+7aq. and 0·8913 grm. $ZnSO_4$+7aq. were added. Another 0·1828 grm. $FeSO_4$+7aq. and 2·25 c.c. standard sulphuric acid were oxidised with nitric acid in platinum dish to dryness on the water-bath, then dissolved in water, and the solution added to the previous mixture, which was diluted to 1 litre, and thoroughly mixed by shaking. This gave a solution equivalent to 10 grms. of a sulphate of the following composition :—

	Per cent.
$Al_2(SO_4)_3$	55·00
Basic Al_2O_3	0·60
$FeSO_4$	1·00
$Fe_2(SO_4)_3$	1·32
$ZnSO_4$	5·00
Water, &c.	37·08
	100·00

Fifty c.c. of this solution, 2 drops methyl indicator, and 100 c.c. water gave for basic alumina 0·6 per cent.

100 c.c., acidified with sulphuric acid, required 1·2 c.c. permanganate solution = 1·02 per cent $FeSO_4$.

100 c.c. + 10 c.c. 6 per cent SO_2 solution + 10 c.c. concentrated sulphuric acid, boiled until free from SO_2, cooled, and diluted, required 2·4 c.c. permanganate solution for total iron. Deducting 1·2 c.c., due to $FeSO_4$, leaves 1·2 c.c. as $Fe_2(SO_4)_3$ = 1·33 per cent.

Fifty c.c. of the solution + 0·6 c.c. were heated to near boiling, then H_2S passed through until cold, the solution left to settle, after which it was filtered, and the precipitate washed thoroughly with freshly prepared and very dilute H_2S water. The clear filtrate was boiled to expel H_2S, cooled, diluted to 150 c.c., 2 drops of methyl indicator added, and the free acid titrated with standard soda solution to orange. Three determinations required 1·25, 1·20, 1·20 c.c.; average, 1·21. This includes acidity due to ferric sulphate, which is equivalent to—

$$\frac{0·132}{400} \times \frac{1}{0·01427} \times \frac{50}{100} = 0·11 \text{ c.c.}$$

standard soda solution, which when subtracted from 1·21 leaves 1·10 c.c due to $ZnSO_4$, and corresponds to—

$$1·10 \times 0·02344 \times \frac{100}{50} = 5·17 \text{ per cent } ZnSO_4.$$

After determining free acid 4 drops of phenol indicator were added, and the titration continued to permanent pink. It required 17·6, 17·5, 17·7 c.c. standard soda solution, or, on an average, 17·6 c.c. This includes basic alumina and total iron as $FeSO_4$, which is equivalent to 0·456 c.c. standard soda solution for the iron, and 0·6 c.c. for the basic alumina, or a total of 1·056 to be deducted from 17·6, which leaves 16·544. This multiplied by 3·33 gives 55·09 per cent $Al_2(SO_4)_3$.

Total results :—

$Al_2(SO_4)_3$	55·09
Basic alumina	0·60
$FeSO_4$	1·02
$Fe_2(SO_4)_3$	1·33
$ZnSO_4$	5·17
Water, &c.	46·79
	100·00

A sulphate of similar composition must not be allowed to stand for any length of time after being made up to a litre, as, on account of the high percentage of iron, insoluble basic ferric sulphates are thrown down, with liberation of sulphuric acid, which will react with the basic alumina and thus make the results too low. Sulphates with such high percentage of iron are hardly ever met with in practice, but was purposely added to this sample in order to show what could be done under such conditions. Should there be less than 5 per cent $ZnSO_4$ in the sulphate, more than 50 c.c. of the solution will be required for precipitation with H_2S, in order to bring the free acid up to a determinable quantity. In that case, the methyl end-point should be compared with a blank, made from pure potash alum and containing approximately the same amount of $Al_2(SO_4)_3$ in an equal volume of water. After determining free acid, a portion equal to

50 c.c. of the original solution should be tested for total sulphates.

The standard soda solution was standardised at 20° C., and the contraction and expansion between 12° and 30° C. were determined by observing the specific gravity between these temperatures. It was thus found that potash alum, which at 20° should test 10·85 per cent $Al_2(SO_4)_3$, would at 12° test 10·83 per cent, and at 30° test 10·87. These variations do not affect the results, as they are less than the probable experimental error.

Another matter which must be borne in mind is that the rate of delivery of standard soda solution must be the same at all times when testing for total sulphates, or the results will vary quite considerably. The slower the delivery, the less standard soda solution will be required to produce the end-point with phenolphthalein. The rate of delivery should therefore be the same as that maintained in standardising the solution against the acid sodium oxalate. A rapid succession of drops is preferable to a full stream. This matter is, of course, not peculiar to this method, but applies to all volumetric work, and is due to the fact that the burette does not recover perfectly; that is to say, the liquid adhering to the sides after a rapid delivery is greater than after a slow one, and will not run down completely, even after several minutes standing, in a burette perfectly clean and free from grease. The necessity for a very slow delivery, when testing for basic, with methyl orange as indicator, must be obvious, as that indicator, in the presence of sulphate of alumina, is by no means instantaneous in its changes. The inaccuracy, due to the delivery, is in that case too small to be noticeable, on account of the small amount of liquid used.

Errors, which usually affect ordinary technical gravimetric alumina determinations, such as neglect to separate silica and metals precipitable by H_2S before precipitating the alumina, and the introduction of silica and alkali from the glass beaker in which the precipitation, as a rule, is made, has no influence on the volumetric determination, and I am convinced, from several years' experience with the method, that the results it gives are much to be preferred to ordinary gravimetric determinations, both as to accuracy and rapidity of execution. Perfectly correct results have been obtained with this method by persons without any analytical training and who could not possibly have made a gravimetric determination.

The ease with which one can accurately determine whether a sulphate is basic, acid, or neutral (normal) will be appreciated by all who for that purpose have had to go through a lengthy gravimetric method.

A NEW CRYSTALLISED SALICYLATE OF BISMUTH.

By PAUL THIBAULT.

We have already described (*Bull. Soc. Chim.*, February, 1901) a method for preparing hydrated oxide of bismuth by means of which this body can be obtained in a state of purity, and, consequently, able to give pure derived salts by the direct union with acids, among others, salicylate of bismuth.

MM. Wolff (*Journ. de Pharm. et de Chim.*, 1884, p. 123), Jaillet and Ragoucy (*Ibid.*, 1884, p. 113), and Causse (*Bull. Soc. Chim.*, 1891, vol. vi., p. 842), have all given different methods for obtaining salicylate of bismuth, either neutral or basic.

With the exception of M. Causse the above writers took nitrate of bismuth, which they treated in aqueous or glycerinated solution with salicylate of soda. Under the conditions described by these authors we have obtained precipitates which in our experiments always contained a constant appreciable amount of nitric acid, about 6 per cent.

M. Causse, in a very ingenious manner, prevented the precipitation of the oxychloride of bismuth by means of a saturated solution of chloride of sodium; he then added a solution of salicylate of soda, rendered alkaline by the addition of caustic soda. The crystalline precipitate we obtained on repeating this experiment contained considerable quantities of chloride, even after ten washings in water containing a little nitric acid. By still further washing we were able to rid the precipitate of all trace of chlorine, but it had then lost its crystalline appearance, and given up all its salicylic acid.

As a matter of fact, all these products are very unstable, and, as M. Thabuis has remarked (*Moniteur Scientifique*, 1895, p. 9), they resist neither the action of water nor alcohol, or even a temperature of 50° C. Further, the analyses of M. Duyck show ("Sur quelques nouveaux médicaments à base de bismuth") that the proportions of mineral oxide and of organic acid contained in the commercial products are extremely variable.

We have not been able to obtain a neutral or basic salicylate of bismuth in a state of purity.

Researches which we have carried out have led us to replace the hydrated oxide of bismuth by the anhydrous oxide obtained in the ordinary manner.

When we mix together either pure or impure hydrated oxide of bismuth with salicylic acid, even in large excess, either cold or at the temperature of the water-bath, we obtain a non-homogeneous product containing both oxide and organic acid uncombined, and some small transparent crystals which resist the action of alcohol.

On the other hand, by using the anhydrous oxide, the whole of it goes into combination at the temperature of the water-bath.

We finally decided on the following method:—15 grms. of crystallised nitrate of bismuth are precipitated in nitric solution by an excess of caustic soda or potash. After boiling, the whole of the amorphous, white, hydrated oxide is transformed into yellow crystallised anhydrous oxide; it is then thoroughly washed, and 10 grms. of salicylic acid rubbed up with 200 c.c. of water are added. The whole is then left on the water-bath for some time; the reaction is a fairly long one to complete, on account of the insolubility of the compound and of its constituents. When at last it is terminated, which can be decided by making sure by means of the microscope that there are no more opaque, yellow needles of anhydrous oxide left, it is decanted hot, thoroughly washed with cold alcohol, and dried in the oven.

In this manner we obtain a very well crystallised salicylate of bismuth, answering to the formula $(C_7H_6O_3)_3Bi_2O_3$.

Analyses gave:—

	Found.	Calculated for, $(C_7H_6O_3)_3Bi_2O_3$.
C	28·39, 28·30, 28·37	28·70
H	1·88, 1·85, 1·90	2·05
Bi	46·60, 46 61, 46·76	47·38
O (by difference)	23·13, 22·94, 22·97	21·87

This substance occurs in the form of a dirty-rose coloured powder, distinctly crystallised in small transparent prisms, acting on polarised light. Water decomposes it slowly in the cold, and more rapidly when hot; water saturated with salicylic acid is without action; cold alcohol also has no action, but when warmed it removes the salicylic acid.

Ether, again, is without action, as is also heat up to a temperature of 140°. If we then continue to apply heat the substance melts with decomposition, becoming black, and giving off phenol. Acids, both hot and cold, separate the salicylic acid, giving the corresponding bismuth salt; the alkalis, potash, soda, and ammonia unite with the salicylic acid, leaving the whole of the bismuth as oxide.

To sum up, we have succeeded in obtaining in a very simple manner by replacing the hydrated oxide of bismuth by the anhydrous oxide, a very well crystallised salicylate

of bismuth answering to the formula $(C_7H_6O_3)_3B_{12}O_3$, undecomposable by cold alcohol, ether, or a temperature of 140°, and acting as a *true salt* of bismuth.

It is, as a matter of fact, as well to make a difference between the *true* salts of bismuth, which on contact with the alkalis part with the whole of their metallic oxides, and other compounds, wrongly called salts, which are completely soluble in the alkalis. We are following up the examination of these different compounds.—*Bull. Soc. Chim.*, Series 3, vol., xxv., No. 16.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending November 30th, 1901.

By SIR WILLIAM CROOKES, F.R.S., and PROFESSOR DEWAR, F.R.S.

To Charles Perrin, Esq., M.Inst.C.E., *Water Examiner, Metropolis Water Act*, 1871.

London, December 10th, 1901.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 202 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Nov. 1st to Nov. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 202 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford has been again considerably below the average; the actual rainfall measured was 0·54 inch, the average is 2·30 inches; this leaves the serious deficiency of 1·76 inches, and, added to the previous deficit of 2·50 inches, makes a total deficiency for the year of 4·26 inches, or 18·4 per cent on the thirty-five years' average.

Our bacteriological examinations of 534 samples have given the results recorded in the following table; we have also examined 38 other samples, from special wells, standpipes, &c., making a total of 572 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	280
New River, filtered (mean of 126 samples) ..	10
Thames, unfiltered (mean of 26 samples) ..	1909
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 292 samples)..	25
Ditto ditto .. .. highest	300
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 26 samples) ..	202
River Lea, from the East London Company's clear-water wells (mean of 38 samples) ..	13

Of the 456 samples of impounded and filtered water supplied to London and examined bacteriologically during the past month, 20 samples, or 4·3 per cent, were sterile. Four samples contained more than 150 microbes, while only fourteen samples, or 3·0 per cent, contained more than 100 microbes per c.c. The mean number of microbes in the fourteen excess samples was 154, against a corresponding mean of 149 in seven excess samples during October.

We may point out that although the amount of rain registered at Oxford is far below the average, such has not been the case with regard to the upper gathering grounds of the Thames Valley. There has been, on the contrary, a considerable amount of rain, though not officially measured, only a few miles above Oxford, and it is the fact that the Thames was in flood, and had overflowed its banks for some miles, towards the end of the month. On the other hand, we are informed that there has only been 0·5 inch of rain during the past eight weeks in the valley of the Lea. The general character of the supply during the month has been decidedly above the average, both chemically and bacteriologically, for the time of year.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

WARNING AGAINST THE USE OF FLUORIFEROUS HYDROGEN PEROXIDE IN ESTIMATING TITANIUM.

By W. F. HILLEBRAND.

Dunnington (*Journ. Am. Chem. Soc.*, vol. xiii., p. 210), has pointed out a source of error to be guarded against in estimating titanium in rocks and minerals by Weller's method, due, as he believes, to the partial reversion, in certain cases, of ordinary titanic to meta-titanic acid, which does not afford a yellow colour with hydrogen peroxide. It remains for me to indicate another source of error in the possible presence of fluorine in the hydrogen peroxide.

For two years the colorimetric method has given reasonable satisfaction in this laboratory, but recently a new lot of hydrogen peroxide was purchased of a different brand from that hitherto used, and after a time it was noticed that the results obtained were in some instances far too high, and that no two determinations agreed.

It is known that hydrogen peroxide does not produce a yellow colour in titanium solutions carrying hydrofluoric acid or fluorides, and moreover the addition of even a drop of the dilute acid to an already peroxidised titanium solution weakens the colour. For this reason it is necessary to take the greatest care to ensure the complete expulsion of all fluorine when dissolving rocks or minerals by means of hydrofluoric and sulphuric acids prior to the colorimetric estimation. A drop of hydrofluosilicic acid acts similarly, but the latter reagent cannot be made to completely discharge the colour even if added in great excess.

This, however, was not suspected as the cause of our trouble until, on referring to the circular of one of the leading makers of hydrogen peroxide in this country, whose product has always given satisfactory results in titanium work, it was found that among the various acids enumerated as usually to be found in the commercial article, hydrofluoric acid appears. Talbot and Moody, in the "Technology Quarterly," v. 123, mention hydrofluosilicic acid as of frequent occurrence in the peroxide manufactured a few years ago. On examining the suspected peroxide by neutralising with fixed alkali, evaporating to dryness, and heating with strong sulphuric acid, fluorine was detected by the odour of the acid evolved and by its action on glass.

It is therefore imperative to use only hydrogen peroxide which is free from fluorine in estimating titanium, for its presence may utterly vitiate the results, even if only 2 or 3 cubic centimetres of the peroxide are employed.—*Bulletin of the United States Geographical Survey*, No. 167.

THE ALKALINE REACTION OF SOME NATURAL SILICATES.

By F. W. CLARKE.

THAT pure water exerts a distinct solvent action upon many natural silicates has long been known. As far back as 1848 the Rogers Brothers published a series of observations upon this subject (*Amer. Journ. Sci.*, Series 2, vol. v., p. 401), and showed that some species of minerals would give an alkaline reaction to test-paper. They did not, however, give details concerning the individual minerals thus investigated. The more recent researches of Daubrée and of Cossa are well known.

By the use of phenolphthalein as an indicator the alkalinity of many silicates can be demonstrated with the utmost ease, and the experiments described below serve to bring out very clearly the relative decomposability of certain minerals and rocks by pure water. The method adopted was as follows:—A series of glass-stoppered bottles was placed against a white background. In each bottle half a grm. of finely pulverised mineral was put, and then 50 c.c. of distilled water, containing a very little alcoholic phenolphthalein, was added. As the indicator was mixed, once for all, with the total amount of water taken for the entire series, the twenty-two samples examined were treated exactly alike. Two of the bottles were filled with the water, and indicator in blank, in order that possible action upon the glass itself might be detected if it occurred. The two blanks, however, remain colourless during the two weeks through which the experiments lasted. The results obtained were as follows:—

Muscovite.—A doubtful trace of coloration, which soon disappeared.

Lepidolite.—Like muscovite.

Phlogopite.—The peculiar non-fluoriferous variety from Edwards, New York. Gave a very distinct, permanent pink colouration.

Orthoclase.—A trace of colouration which increased for a few days, and then faded.

Oligoclase.—The transparent variety from Baskerville, North Carolina. Distinct and permanent, but pale colouration.

Albite.—From Amelia County, Virginia. Gave a good, permanent, alkaline reaction.

Leucite.—A slight reaction at first, which faded in a few days.

Nephelite.—The elæolite from Litchfield, Maine. Good colouration, but partly fading in time.

Cancrinite.—Litchfield, Maine. Gives a deep rose colouration, which is permanent.

Sodalite.—From Canada. A deep, permanent rose colour.

Spodumene. — The transparent, yellow variety from Brazil. A good reaction, but gradually fading.

Scapolite.—The wernerite from St. Lawrence County, New York. Gave a faint, evanescent trace of colouration.

Laumontite.—A doubtful trace of colouration.

Stilbite.—Faint, evanescent colouration.

Chabazite.—Like stilbite.

Heulandite.—Slight reaction, but distinct.

Thomsonite.—Variety lintonite. A fairly strong reaction, fading in time.

Analcite.—Good alkaline reaction.

Natrolite.—From Bohemia. Strong colouration, permanent.

Pectolite.—From Bergen Hill. Gave a very deep rose colour.

Apophyllite.—From Bergen Hill. A very deep rose colour.

In nearly every case the reaction was obtained at once, showing a more rapid action of water upon the silicate than had been anticipated. In some instances fading is noted. This is doubtless due, in general, to the action of light, but in certain cases the coloured solution separated into two layers, the colour being wholly in the lower. Here the colour was really held as a coating upon the fine solid particles, and as they subsided the appearance of stratification was produced. Toward the end of the experiments the mineral aegirite was added to the series. This also gave a strong alkaline reaction, and a fairly deep rose colour.

A neat method of demonstrating the reactions described above is the following:—Place a little of the mineral to be tested in a watch-glass upon a sheet of white paper. Add a drop of alcoholic phenolphthalein solution, and then a few drops of pure water; in most cases the reaction is given instantaneously. Orthoclase gave no colouration, leucite a trace, and scapolite a trace; albite, nephelite, and phlogopite furnished distinct reactions. Under the same circumstances thomsonite, aegirite, natrolite, cancrinite, sodalite, pectolite, and apophyllite, gave immediately a deep, rich, rose colour. The strongest alkaline reactions seemed to be given by pectolite and apophyllite.

In general the order of intensity of the colour produced was what might have been expected. Among the micas, muscovite and lepidolite showed little or no solubility, while phlogopite was distinctly attacked. In nature the magnesian micas are far more easily alterable than muscovite, a fact which is reiterated by these experiments. Again, orthoclase was slightly dissolved, albite much more so, and oligoclase gave a reaction between the two; that is, more than the one, less than the other. In other words, the plagioclase felspars alter more easily than orthoclase, as is apparent in the study of the rocks themselves.

In order to bring out the latter point more clearly, a series of rocks which had been analysed in the laboratory of the United States Geological Survey was placed in a row of bottles, and treated, just as the mineral species had been, with water and phenolphthalein. A granite and an amphilbole-gabbro gave no alkaline reaction. A rhyolite, trachyte, leucite-basalt, felspar-basalt, and diorite gave faint traces of colour. Granitite, gneiss, phonolite, diabase, and camptonite yielded distinct alkaline colourations.

In all of these instances the production of colour is doubtless due to the solution from the mineral or rock of alkaline silicates. The noteworthy point is the quickness with which the reaction can be obtained. With minerals like cancrinite, sodalite, natrolite, pectolite, and apophyllite, the reaction is striking enough to be used as a lecture-table experiment.—*Bulletin of the United States Geological Survey*, No 167.

THE QUANTITATIVE DETERMINATION OF CADMIUM.*

By EDMUND H. MILLER and ROBERT W. PAGE.

THE work described in this paper was suggested by the difficulties encountered in some experiments on the determination of cadmium, which were undertaken before analysing a number of precipitates of cadmium ferrocyanide. The methods compared are the electrolytic, the carbonate, and the phosphate. The work was done on a solution of cadmium chloride, found to be free from impurities, which after thorough mixing was sealed up in a number of bottles to avoid evaporation.

Electrolytic Determination.

The cyanide method (Riban, "Analysis Chimique Quantitative par Electrolyse," Paris, 1899; Rimbach, *Zeit. f. Anal. Chem.*, 1898, xxxvii., p. 284), was used under the following conditions:—Thirty c.c. of the cadmium chloride solution were diluted to 150 c.c. and 1

* Contribution from the Havemeyer Laboratories of Columbia University. From the *School of Mines Quarterly*, xxii., No. 4.

grm. of potassium cyanide added, this amount being a slight excess over that required to re-dissolve the cadmium cyanide first formed. The solution was then electrolysed by a current of 0·1—0·15 ampere for sixteen hours. The kathode was a platinum cylinder having an area of 90 square c.m., the anode a spiral of heavy platinum wire. The deposition was found to be complete in every case, the electrolyte was colourless, and the deposited metal bright and adherent. The results are given in Table I.

Average weight of cadmium, coinciding with three determinations, 0·2088.

It was found that a large excess of potassium cyanide was to be avoided and also the presence of other salts. When cadmium is separated as sulphide and then dissolved in hydrochloric acid, the excess should be removed by boiling and not be neutralised by sodium carbonate, as the resulting sodium chloride interferes with the electrolytic precipitation. Three grms. of potassium cyanide under the preceding conditions gave results which were lower and less uniform.

The Carbonate Method.

This method was used merely as a check on the electrolytic results before proceeding to the phosphate determination. The cadmium chloride solution was precipitated by a slight excess of sodium carbonate, boiled, and the precipitate washed till it gave no evidence of alkali when tested with phenolphthalein; dried, separated from the paper, &c., ignited, and weighed as cadmium oxide. The results expressed in grms. of cadmium were 0·2098, 0·2106, 0·2087. These are fairly satisfactory considering the difficulties of the method, and serve to confirm the accuracy of the results obtained by electrolysis. So the strength of the cadmium solution is taken to be 0·2088 grm. of cadmium in 30 c.c., the amount used throughout.

The Phosphate Method.

Drewsen ("Gmelin-Kraut Handbuch," 6th Auflage, III., 74), is apparently the only authority for giving to the cadmium ammonium phosphate 1½ molecules of water of crystallisation. So before starting work upon this method it seemed advisable to make a series of experiments to verify this statement in order that determinations could be made by weighing the cadmium ammonium phosphate as well as the pyrophosphate. Eight determinations were accordingly made, and the results show that there is an even molecule of water present, just as is the case with the double ammonium salts of manganese and cobalt (Dakin, *Zeit. für. Anal. Chem.*, Dec., 1900). These determinations were made as follows:—The precipitates, thrown down by either microcosmic salt or by the diammonium phosphate, were dried to constant weight at 100—103° C. It was found that the weight remained practically constant up to 110° C. and then diminished rapidly, so that it was not safe to use a temperature above 105° C. in drying. After obtaining the weights at 100—103° C. the precipitates were ignited and weighed as pyrophosphate, and from these two weights the molecular weight of the $CdNH_4PO_4xH_2O$ was calculated. The results were all between the limits of 242·64 and 244·4 compared with 243·85, the molecular weight of $CdNH_4PO_4H_2O$. The average result was 243·79, corresponding to 1·016 molecules of water.

The only information on the quantitative estimation of cadmium as phosphate is in a recent paper by Austin (*Am. Journ. Science*, 1899, 158, 214; also *Zeit. für Anorg. Chemie*, 1899, 22. 207); it concludes thus:—

"Cadmium may be estimated with accuracy as the pyrophosphate if the precipitate by microcosmic salt in the nearly neutral solution containing ammonium chloride in the proportion of 10 grms. to 100 c.c. is allowed to stand several hours before filtering. In this way all the cadmium separates out from the solution as a beautiful crystalline mass of cadmium ammonium phosphate of ideal constitution. The conditions must, however, be preserved with care; there must be no excess of ammonia,

TABLE II.

No.	Cadmium taken, in grm.	$CdNH_4PO_4H_2O$ found, in grm.	$CdNH_4PO_4H_2O$ in terms of cadmium.	Error, in grm. of cadmium.	$Cd_2P_2O_7$ found, in grm.	Error, in grm. of cadmium.	NH_4Cl in grms.	Filtrate with H_2S.	Remarks.
1.	0·2088				0·3194	−0·0288	15	Heavy ppt. of CdS	Austin's conditions.
2.	0·2088				0·3392	−0·0177	15	"	"
3.	0·2088				0·3391	−0·0177	15	"	"
4.	0·2088				0·3373	−0·0180	15	"	"
5.	0·2088				0·3403	−0·0170	15	"	"
6.	0·2088				0·3425	−0·0158	15	"	"
7.	0·2088	0·4295	0·1982	−0·0106			15	Austin modified.	
8.	0·2088	0·4328	0·1997	−0·0091			15	"	"
9.	0·2088				0·3764*	+0·0033	1	Trace	Dakin's conditions.
					0·3698†	−0·0004			
10.	0·2088				0·3758	+0·0029	1	Trace	
					0·3692	−0·0008			
11.	0·2088				0·3747	+0·0023	1		
					0·3692	−0·0008			
					0·3725	+0·0011	1		
12.	0·2088				0·3693	−0·0007			
		0·4510	0·2082	−0·0006				Balance papers heated in ½ hour.	
13.	0·2088	0·4525	0·2088	—					
14.	0·2088	0·4524	0·2088	—					
15.	0·2088	0·4531	0·2091	+0·0003	0·3701	+0·0002			
16.	0·2088	0·4525	0·2088	—	0·3696	−0·0004			
17.	0·2088	0·4532	0·2091	+0·0003	0·3722	+0·0009		Balance papers ppt. in cold.	
18.	0·2088	0·4524	0·2088	—					
19.	0·2088	0·4524	0·2088	—					
20.	0·2088	0·4530	0·2091	+0·0003	0·3712	+0·0004			

* By re-weighing after dissolving through with nitric acid.

† By direct weight on asbestos in Gooch crucible.

no free acid, and no excess of ammonium salt beyond the quantity indicated, while that amount is necessary."

A series of determinations was made following Austin's directions as closely as possible; the results were invariably low, and on testing the filtrate with hydrogen sulphide a heavy precipitate of cadmium sulphide was always obtained. (See Table II.)

Instead of experimenting further with Austin's conditions, a more promising field seemed to be the adaptation of the conditions given by Dakin (*Zeit. für. Anal. Chem.*, 1900, 39, 273), for the precipitation of zinc ammonium phosphate to the determination of cadmium. The essential differences are the use of ammonium phosphate instead of microcosmic salt, and the absence of the ammonium chloride held to be so necessary by Austin for the precipitation of either zinc or cadmium.

The next series of determinations (Nos. 9 to 12, Table II.) were made following exactly Dakin's conditions. The cadmium chloride solutions were diluted to a bulk of 150 c.c. and 0·5 c.c. of hydrochloric acid added, and then nearly neutralised with ammonia; then heated on a water bath and 35 c.c. (2·6 grms.) of ammonium phosphate solution added, and the heating continued for fifteen minutes. The phosphate solution was made exactly according to Dakin's directions and contained 80 per cent of $(NH_4)_2HPO_4$ to 20 per cent of $NH_4H_2PO_4$. After warming, the precipitates were allowed to stand over night before filtering; they were flocculent at first, became partly crystalline on warming, and after standing over night consisted entirely of large scale-like crystals of a pearly lustre, which settled immediately and were readily washed. They were filtered on asbestos in a Gooch crucible and washed first with a 1 per cent solution of the precipitant, then with 60 per cent alcohol, next dried and finally ignited, using a low flame at first, to pyrophosphate, and weighed.

As the asbestos used by Dakin was slightly soluble in the ammonium phosphate, he determined the weight of the Gooch crucible after weighing the precipitates—dissolving out the pyrophosphate with dilute nitric acid. The results in the table give both methods of procedure, direct weight and by difference. The determinations made by dissolving out the precipitate are invariably high, while those made by direct weight are slightly low. These figures lead to an investigation of the solubility of the asbestos in nitric acid as well as in the phosphate solution, which showed constant loss with either solution, even where the asbestos had been treated first with boiling nitric acid and then been allowed to stand one portion with nitric acid, the other with a strong ammonium phosphate solution for two weeks, and explained satisfactorily the error in using an asbestos filter.

To avoid this source of error a series of determinations was next made in which the precipitates were filtered on balance papers. This precipitate is particularly well adapted to this method, as the crystals are large, easily washed, and show no tendency to creep or run through. The reagent used was 100 per cent $(NH_4)_2HPO_4$, which we believe better than the mixture used by Dakin, as the dihydrogen ammonium salt gives no precipitate with cadmium. It is easily obtained by adding ammonia to the purchased reagent till it gives a slight pink with phenolphthalein.

The conditions for precipitation were as follows:—

To the cadmium chloride solution diluted to 150 c.c. and barely acid with hydrochloric acid add 35 c.c. (2·9 grms) of $(NH_4)_2HPO_4$ about fifteen times the weight of the cadmium prssent, and allow to stand over night. In Nos. 13—16 (see Table II.) the precipitant was added to the warm solution and then heated on a water-bath for fifteen minutes. This practice, while causing the conversion to the crystalline condition to take place more rapidly, is not to be recommended, as there is danger of the composition of the precipitate being changed by loss of ammonia. The precipitation is best made in the cold (Nos. 17—20), then allowed to stand over night.

TABLE I.

No.	Solution taken, c.c.	KCN, in grm.	Ampèrage.	Time, in hours.	Bulk, in c.c.	Cadmium in grm.
1.	30	1	0·15	16	160	0·2088
2.	30	1	0·15	16	160	0·2088
3.	30	1	0·15	16	160	0·2090
4.	30	1	0·1—0·15	16	160	0·2089
5.	30	1	0·1—0·15	16	160	0·2086
6.	30	1	0·1—0·15	16	160	0·2088

TABLE III.

No.	Cadmium taken, in grm.	Weight of precipitate dried at 100—103° C.	Cadmium calculated from $CdNH_4PO_4H_2O$.	Error, in terms of cadmium.
1.	0·2088	0·4427	0·2044	−0·0044
2.	0·2088	0·4382	0·2025	−0·0063
3.	0·2088	0·3965	0·1830	−0·0258
4.	0·2088	0·3715	0·1715	−0·0373
5.	0·2088	0·3430	0·1583	−0·0505
6.	0·2088	0·3429	0·1583	−0·0505
7.	0·2088	0·3306	0·1526	−0·0562
8.	0·2088	0·3346	0·1544	−0·0544

Remarks.

Nos. 1 and 2.—Heated one hour and filtered at once.
Nos. 3 and 4.—Heated on water-bath one hour.
Nos. 5 and 6.—Boiled gently one hour.
Nos. 7 and 8.—Boiled moderately.

TABLE IV.

	Theory for $CdNH_4PO_4H_2O$.	Crystalline precipitate.	Pulverulent precipitate.
	Per cent.	Per cent.	Per cent.
NH_3	7·00	6·75	0·48
H_2O..	11·09	10·83	1·47
P_2O_5	22·16	29·40	24·31
CdO..	52·75	52·83	73·56
	100·00	99·81	99·82

Precipitates 13—20 were all filtered on balance papers (after drying at 105° C. for several hours), washed first with a 1 per cent solution of $(NH_4)_2HPO_4$, then with 60 per cent alcohol, and weighed after drying to constant weight at 100—103° C.

In Nos. 15, 16, 18, and 20 the precipitates were dissolved in dilute nitric acid, evaporated and ignited in platinum to $Cd_2P_2O_7$. Weighing as $CdNH_4PO_4H_2O$ is to be preferred, as it is shorter and the danger of reduction and volatilisation is avoided. These results are shown in Table II.

The next series was made to determine the effect of ammonium chloride, as this salt is likely to be present in varying quantities. The conditions were identical with Nos. 17—20 in Table II., except that each solution contained 15 grms. of ammonium chloride. The results expressed in grms. of cadmium were 0·2080, 0·2082, 0·2081, 0·2083. The filtrates gave in each case a slight but distinct precipitate of cadmium sulphide when tested with hydrogen sulphide. These results show that ammonium chloride, in any such quantity, exerts a slight solvent action, and is to be avoided when great accuracy is required.

The effect of heating on the precipitate was next investigated, and the results given in Table III.

The danger, already mentioned, of hastening the conversion to the crystalline condition by heating is fully shown by Table III. In Nos. 1 and 2 the $CdNH_4PO_4H_2O$ precipitates were heated one hour in a water-bath, until they were entirely crystalline, and then filtered at once; the other conditions were the same as Nos. 13—20 in Table II., where accurate results were obtained. The physical properties of the precipitates were changed by the heating, the crystals were finer, and a portion of the pre-

cipitate was decidedly pulverulent. Nos. 3 and 4 were heated at a higher temperature on the water-bath until the precipitates became crystalline, and then stood over night before being filtered. In these, a larger proportion of the pulverulent precipitate was noticed. Nos. 5 and 6 were boiled gently; here the precipitates consisted chiefly of the dense pulverulent particles with a small quantity of coarse scale-like crystals resembling those formed in the cold. In Nos. 7 and 8 the boiling was more vigorous, and here the precipitates were entirely pulverulent, and in no way resembled those obtained in the cold.

This change in appearance, together with the low results, indicate certainly a change in the composition of the precipitate. Ammonia is given off in noticeable quantities during the boiling.

The coarse crystalline precipitate formed in the cold, and the fine pulverulent precipitste, made by boiling small quantities in separate beakers, on account of great trouble due to bumping, were analysed, with the results given in Table IV.

The analyses show the loss of both water and ammonia by boiling, and suggests that the normal cadmium orthophosphate would be produced were the boiling sufficiently prolonged, and at the same time confirm the determination of the water of crystallisation in the crystalline precipitate.

The points which we wish to emphasise are:—

1. That the electrolytic determination of cadmium is most accurate and satisfactory, provided a large excess of potassium cyanide and the presence of other salts are avoided.

2. That the carbonate method is the most troublesome, and the least accurate.

3. That cadmium ammonium phosphate contains one molecule of water of crystallisation, and can be dried without decomposition at 100—103° C.

4. That Austin's method for cadmium is unsatisfactory.

5. That asbestos filters should be avoided on account of the solvent action of either ammonium phosphate or nitric acid.

6. That cadmium can be determined with great accuracy by precipitating in the cold, in a neutral solution by a large excess of $(NH_4)_2HPO_4$, and allowing to stand over night; it can be weighed on balanced filters or ignited to pyrophosphate. If precipitated in a boiling solution or on prolonged boiling it is liable to change in composition and give low results.

We recommend this method as preferable to the carbonate method in all respects, and while no more accurate than the electrolytic, it has the practical advantage of requiring no extraordinary or expensive apparatus.

NOTICES OF BOOKS.

Engineering Chemistry. A Manual of Quantitative Chemical Analysis for the Use of Students, Chemists, and Engineers. Second Edition. By Thomas B. Stillman, M.Sc., Ph.D. With 132 Illustrations. Easton, Pa.: The Chemical Publishing Company, 1900. Pp. 503.

This valuable work is not intended for beginners, as may be gathered from the title. Students commencing quantitative work can perform (as the author tells us), with advantage, the first eleven exercises given in this work with proper supervision, and then select a course of study suitable to their advancement; either for iron and steel chemistry; railroad laboratory practice; the technical application of water supply; the chemical technology of fuels, &c.

These eleven exercises referred to comprise such typical examples as the determination of iron in iron-wire, of alumina in potash alum, of lead in galena, of iron in hematite, of phosphorus pentoxide in calcium phosphate, &c.

The articles upon gas analysis and valuation, blast-furnace practice, the heating value of fuels, the purification of water for technical purposes, lubrication, car illumination, and the examination of Portland cement, have all received special attention, since these topics, at the present time, form a considerable portion of the work and investigations of engineers; a number of articles on the above subjects have been contributed by experts in each line of study.

As is only too often the case in books of this class, the section devoted to water analysis is incomplete and old-fashioned. The untrustworthy and discredited method of estimating the organic matter in water by the "albumenoid ammonia" process is given in full, while no mention is made of that beautiful and exact method devised by the late Sir E. Frankland and Prof. Armstrong, known as the "combustion process." It is true that the latter method requires more expensive apparatus than does the former, but that should not be a drawback in a properly equipped laboratory; probably the reason why the combustion process is so often neglected lies in the fact that it requires much more intelligence and manipulative skill for its proper performance, but that *again* should be no drawback in a properly conducted laboratory.

The book is well arranged and printed, and its value as a whole is considerable; it should indeed be found in all commercial laboratories. It is provided with a very extensive table of contents and a large index.

Handbook of Practical Hygiene. By D. H. Bergey, A.M., M.D., Easton, Pa.: The Chemical Publishing Company. Pp. 164.

The object for which this book was prepared was to afford a help to students in the sanitary analysis of air, water, soil, and the principal food materials, and in testing the ventilation of buildings, &c. There are several excellent hand-books on these subjects in German, as well as a number of general treatises on hygiene in English, but there has been a lack of any short concise laboratory guide.

Here as a general rule only the more simple and ready methods now in use have been used. The subject of food analysis has been gone into far enough to permit the detection of the more common forms of adulteration that are likely to be met with.

The book is divided into five parts, viz.:—I. Atmospheric air; II. Water; III. Soil; IV. Sanitary Analysis of Foods, and V. Ventilation and Heating, and each part is again sub-divided into several chapters.

With regard to the chapters on water analysis we may point out that the old-fashioned, untrustworthy albumenoid ammonia method has been given undue prominence, while the best and most delicate method is entirely neglected. There are a good number of the most modern methods given for estimating nitrogen as nitrates and nitrites, but none of them compare with the old indigo method for speed and simplicity.

The book has been very carefully compiled, and will well repay perusal not only by the student but by the practical analytical chemist as well.

Die Chemische Organisation der Zelle. By Dr. F. Hofmeister. Braunschweig: Friedrich Viewig und Sohn.

In this paper, which was written for the Hamburg Scientific Society, an attempt is made for the first time to elucidate the structure of protoplasm by investigating the chemical processes occurring in the cell. The author believes that a fuller knowledge of the chemistry of these processes and of the substances elaborated by them will do more towards solving the problem of the essential nature of living protoplasm than the most careful micro-

scopic work, though he by no means under estimates the value of the latter method. Bearing in mind Dr. Hofmeister's distinguished researches on pepsin and the peptones, we have every reason for believing in his ability to throw light upon this more complex and extended question. Taking the liver cell as a typical example, he enumerates the various substances produced by it, such as bilirubin and cholic acid, the exact composition of which is yet to be determined, and dwells upon the theory of the probable existence in the cell of a ferment corresponding to each chemical process, and the recent discoveries of the power of the animal body to create antidotes, antitoxins, &c. Many of the ideas contained in the paper are original, and though written chiefly from a physiological point of view, the chemist will find in it much to interest him and to suggest profitable subjects for research.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 23, December 2, 1901.

Induced Radio-activity provoked by Radium Salts.—P. Currie and A. Debierne.—It is known that all bodies become radio-active when they are enclosed in a vessel containing a solid salt of radiferous barium. This radio-activity said to be induced, can also be obtained by replacing the solid radium salt by an aqueous solution, and the effects produced are more regular by this latter method. The various solid bodies experimented with (copper, platinum, lead, tin, aluminium, glass, paper, wax, zinc sulphide, &c.), acquire the same activity when placed in contact with the exciting agent, under the same conditions. The radiating power of the bodies is, in the same manner as radium itself, composed of rays deviated or non-deviated by the magnetic field. The induced activity is independent of the pressure and the nature of the gas surrounding the exciting agent. Certain substances (those phophorescent to light and others) become luminous when placed in contact with radium, zinc sulphide being especially brilliant under these conditions. Glass also acquires phosphorescent properties, especially Thuringen glass. The limit of activity produced with the same exciting agent depends only on the quantity of radium which is in solution.

Influence of Radio Active Substances on the Luminescence of Glass.—Alix de Hemptinne.—Some time ago the author discovered that a gas which becomes luminous when subjected to a certain pressure under the influence of electric vibrations becomes luminous at a higher pressure under the influence of X-rays. He now establishes the fact that if a tube containing rarefied gas, through which an electric current is passing, is brought near some of the radio-active materials, the gas becomes luminous at a pressure of 44 m.m., while away from the exciting agent it does not become luminous until a pressure of 33 m.m. is produced. Also the colour, which was a red-violet in the latter case, becomes yellowish green under the influence of radio-active substances.

Study of the Tin-Aluminium Alloys.—Léon Guillet.—Tin-aluminium alloys have been investigated by M. Gautier, but chiefly from the point of view of fusibility. So far, however, no compounds of tin and aluminium have been isolated. The curve of fusibility predicts the compound $AlSn$. The author was able to isolate the two compounds Al_4Sn and $AlSn_2$ in the crystalline state and also in the state of a crystalline powder. All the experiments were made on 3 kilos. of material, but the volatilisation of the tin rendered the experiments difficult. Tin estimations were made electrolytically. These experiments lead to the conclusion that—(1) All the reactions are extremely violent, and there are enormous losses of tin in the form of stannic acid. (2) The limiting compound formed is Al_4Sn. (3) All experiments containing more tin than that corresponding to $AlSn_5$ leave no metallic residue. (4) All the portions of alloy contain considerable quantities of free aluminium (6 per cent to 13 per cent). (5) The quantity of tin in the alloy does not increase regularly with the initial quantity employed.

Action of Pyridic Bases on Tetrahalogenated Quinones.—Henri Imbert.—The oxidation derivative of the body $C_5H_4N—C_6Cl_2O_2—OH$, the preparation of which has already been described by the author, and of which the percentage composition corresponds to the formula $HO—C_5H_2N=C_6Cl_2O_2$ shows that the formulæ is the correct one. An examination of two derivatives of the primitive body show the existence of three ketonic functions, of which two neighbours, in a trichlorotriketopentamethylenic radicle, analogous to that which Hantzsch obtained during the oxidation of chloro and bromanilic acids. The chlorohydrate of pyridyltrichlorotriacetopentamethylene gives the possibility of a choice between the two conceivable formulæ, to represent the derivatives proving the ctaion of pyridic bases on tetrahalogenated quinones, $C_5H_4N—C_6Cl_2O_2—OH$ or $HO—C_5H_2N=C_6Cl_2O_2$, for only the first agrees with the formation of the preceding derivatives.

Bulletin de la Société Chimique de Paris. Series 3, Vol. xxv., No. 13.

Researches on the Oxides of Chlorine.—A. Reychler.—Already inserted in full.

Peroxide of Chlorine as a Sterilising Agent for Potable Waters.—A. Reychler.—To 5 litres of water, a calculated quantity of a freshly prepared solution of the peroxide was added, so as to form a solution containing 0·003 grm. of ClO_2 per litre, equal to 2·22 c.c. of decinormal thiosulphate. After thirty-five minutes the water was coloured distinctly blue by starch emulsion. The chlorometric value per litre was then 1·51 c.c. of thiosulphate. After two hours thirty minutes, the blue colour was less intense and the titration value was 1·5 c.c. of thiosulphate. After seven hours thirty minutes, there was a violet-rose colour and the titration required 1·41 c.c. of thiosulphate. After twenty-three hours, there was only a faint rose colour and only 1·37 c.c. of thiosulphate were required. The chlorometric value had therefore decreased to six-tenths of its original figure.

Aluminate of Magnesium.—Em. Dufau.—Already inserted in full.

Hydrogenation of the Incomplete Carbides in the presence of various finely-divided Metals.—P. Sabatier and J. B. Senderens.

Action of various finely-divided Metals on Ethylene and Acetylene.—P. Sabatier and J. B. Senderens.

Secondary Products formed in the Action of Sulphuric Acid on Wood-Charcoal.—A. Verneuil.

Myrcenol and its Constitution.—P. Barbier.—These four papers have been already noticed.

MEETINGS FOR THE WEEK.

Tuesday, Dec. 31, 1901.	Royal Institution, 3. (Christmas Lectures to Young People). "On Waves and Ripples in Water, Air, and Æther," by Professor J. A. Fleming, M.A., F.R.S., D.Sc.
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